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X-RAY CRYSTAL STRUCTURE OF A TERNARY COPPER(II) PEPTIDE CREATININE COMPLEX, (AQUO)(CREATININE)(GLYCYLGLYCINATO) COPPER(II) SESQUIHYDRATE

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Abstract—The first creatinine ternary complex $[Cu(gg)(H_2O)(creat)] \cdot 1.5\ H_2O$ (**1**) [gg = glycylglycine (2−), creat = creatinine] has been crystallized from aqueous solution. The coordination geometry about the copper is approximately square pyramidal with the tridentate glycylglycine dianion and the N(1) of creatinine occupying the corners of a square. The coordination sphere about the copper is completed by an axial water molecule, Cu—OW(1) distance 2.496(2) Å. Another water molecule OW(2), Cu—OW(2) distance 2.907(2) Å, extends qualitatively the coordination geometry to octahedral. A third water molecule OW(3) with an occupancy factor of 0.5 is disordered and is located between two complex units. The complete crystal structure is maintained by an extensive hydrogen-bonding network in which the three types of water molecules are involved.

The important role played by ternary copper(II) complexes in biological systems is well known.[1] Metal ions are known to promote specific protein–nucleic acid interactions through the formation of ternary complexes.[2] Nucleic acid–enzyme ternary complexes are formed with M^{II} cations during DNA replication, while Cu^{II} ions, for example, mediate polypeptide–polynucleotide interactions.[3] In spite of this, few studies have been devoted to the crystal structure of peptide/nucleic acid component ternary complexes.[4] In the same way, mixed-ligand complexes have received much attention because they could mimic substrate–metal ion–enzyme interactions in the active centre of enzymes.[5]

Several ternary complexes involving amino acids and small peptides were detected in human serum, which could play an important role in the exchange of Cu^{II} between a macromolecule (HSA) and low molecular-weight complexes capable of being readily transported across the biological membrane.[6]

On the other hand, although urinary copper excretion is negligible under normal conditions, a small fraction of ingested copper that does appear in urine comes from the amino-acid bound fraction of plasma copper.[1b] Since the bioligand creatinine (Fig. 1), the final catabolic product of creatine, which plays an important role in protein metabolism, is present in serum and urine,[7] we have focused interest on the study of the specific interactions between the glycylglycinato–Cu^{II} system and this ligand. Several authors[8] have suggested that an understanding of the metabolic pathways of creatine can be achieved through the study of

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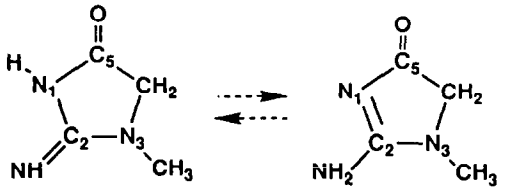

Fig. 1. Tautomeric forms of creatinine.

the interactions between creatinine and metal ions. Previous crystallographic investigations of metal complexes of creatinine have demonstrated that creatinine normally binds to the metal ion through the ring N(1) atom,[9] although chelation through the exocyclic and ring nitrogens[10] and exocyclic O(5)[11] binding also have been observed.

In this context we report here the synthesis, spectroscopic characterization and X-ray structure of a ternary peptide creatinine complex: [Cu(gg)(H_2O)(creat)] · 1.5 H_2O (**1**).

EXPERIMENTAL

Analyses and physical measurements

Analytical measurements were carried out using a Carlo Erba model 1106 microanalyser. The IR spectra were registered in the solid state (KBr pellets) on a PE 683 with an IR data station PE 1600 and the electronic spectra were registered on a PE 552 spectrophotometer. Thermogravimetric and DSC data in the temperature range from 30 to 700°C were recorded in flowing nitrogen (heating rate 2°C min^{-1}) on a PE TGA-2 thermobalance and PE DSC-4 system. Crystallographic studies were performed on an Enraf–Nonius CAD 4 diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å). Creatinine was obtained from Fluka and glycylglycine from Aldrich. Both products were used without further purification. The preparation of diaquo glycylglycinato copper(II) followed essentially from the method of Manyak *et al.*[12a]

Preparation of [Cu(gg)(H_2O)(creat)] · 1.5 H_2O

A sample (0.5 mmol) of creatinine was added to a solution of diaquo glycylglycinato copper(II) (0.5 mmol) in distilled water (10 cm^3). The resulting solution was heated on a steam bath (75°C) for 0.5 h and subsequently concentrated in a rotating evaporator (at 50°C) to a 5 cm^3 volume. After 3 days, blue rhombic crystals were obtained by slowly diffusing ethanol into the concentrated solution of the complex. The complex obtained exhibits a weight loss between 70 and *ca* 190°C corresponding to the loss of two and a half water molecules per formula unit (mass loss calc. 12.8%, mass loss found 12.5%). The dehydration process takes place in only one step, which is clearly seen in the DSC diagrams of the ternary complex and glycylglycinato copper(II) trihydrate complex[13] as endothermic effects at 107°C and 106°C (T_{max}), and 197.875 and 321.875 J g^{-1} (energies), respectively. Found: C, 27.4; H, 5.1; N, 19.6. Calc. for $C_8H_{15}N_5O_5Cu \cdot 1.5\ H_2O$: C, 27.3; H, 5.1; N, 19.9%. IR (cm^{-1}): 296w, 350w, 439w, 601m, 670m, 702m, 861w, 929w, 997m, 1029m, 1052m, 1130m, 1205w, 1218w, 1240m, 1296m, 1344m, 1374s, 1423m, 1455m, 1507m, 1580s, 1620s, 1674s, 1713m, 3113s, 3250–3260s, br, 3359s, 3408s, sh. $\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$ of 10^{-3} M in MeOH, 20°C = 16. $\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$ of 10^{-3} M in H_2O, 20°C = 31.

X-ray data collection and structure determination

Cell parameters were obtained by least squares refinement of 22 reflections on an Enraf–Nonius CAD-4 diffractometer.[14] A summary of the crystal and structure refinement data is shown in Table 1. Mo-K_α radiation monochromatized by reflection from a graphite crystal was used for data collection. Using the ω–2θ technique, 4440 reflections were collected ($2\theta < 61°$), of which 4143 were unique ($R_{int} = 0.015$) and used in the further refinement. Lorentz–polarization and empirical absorption corrections were applied (max. and min. transmission factors 0.9998 and 0.8710).

The structure was solved by direct methods with the MULTAN 11/82[15] program using the MolEN package.[14] Subsequent weighted Fourier syntheses gave the remaining non-hydrogen atoms. Full-matrix refinement on F^2 was carried out with the SHELX93 least-squares program[16] using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were refined riding on their bonded atoms with a global isotropic temperature factor. The refinement process converged at $R_1[I > 2\sigma(I)] = 0.030$, wR_2(all data) = 0.088, using 219 variable parameters. Scattering factors were taken from *International Tables for X-Ray Crystallography*,[17] except for those of hydrogen atoms.[18] The largest shift/e.s.d. value in the final cycle was 0.104. Maximum and minimum final difference Fourier map peaks are 0.42 and −0.34 e $Å^{-3}$.

Selected bond lengths and bond angles are given in Table 2. Figure 2 shows a perspective view of the complex with the atom numbering, which was depicted using ORTEPII.[19]

Table 1. Crystal data and structure refinement

Complex	[Cu(gg)(H_2O)(creat)]
Formula	$C_8H_{13}N_5O_4Cu \cdot 2.5H_2O$
Formula weight	351.81
Temperature (K)	294(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.317(1)
b (Å)	7.349(2)
c (Å)	14.167(1)
α (°)	87.68(1)
β (°)	84.94(1)
γ (°)	64.27(1)
V (Å^3)	683.6(2)
Z	2
D_c (g cm^{-3})	1.709
Absorption coefficient (mm^{-1})	1.636
$F(000)$	364
Crystal colour, habit	blue, rhomboidal
Crystal size (mm)	0.39 × 0.31 × 0.06
θ range for data collection (°)	2.9–30.4
Index ranges	$-10 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 0$, $-20 \leqslant 1 \leqslant 20$
Reflections collected	4440
Independent reflections	4143 (R_{int} = 0.0147)
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4143/219
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0298, wR_2 = 0.0782
R indices (all data)	R_1 = 0.0569, wR_2 = 0.0878
Largest diff. peak and hole (e Å^{-3})	0.416 and −0.342

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Cu(1)—N(7)	1.907(2)
Cu(1)—N(1)	2.014(2)
Cu(1)—N(9)	2.022(2)
Cu(1)—O(6)	2.0338(14)
Cu(1)—OW1	2.496(2)
Cu(1)—OW2	2.907(2)
O(5)—C(5)	1.220(2)
O(6)—C(6)	1.276(2)
O(7)—C(6)	1.239(2)
O(8A)—C(8)	1.360(4)
O(8B)—C(8)	1.257(4)
N(1)—C(2)	1.367(2)
N(1)—C(5)	1.375(2)
N(2)—C(2)	1.320(2)
N(3)—C(2)	1.331(2)
N(3)—C(4)	1.443(2)
N(3)—C(3)	1.446(2)
N(7)—C(8)	1.298(2)
N(7)—C(7)	1.438(2)
N(9)—C(9)	1.438(3)
C(4)—C(5)	1.515(2)
C(6)—C(7)	1.526(2)
C(8)—C(9)	1.506(3)
N(7)—Cu(1)—N(1)	176.88(6)
N(7)—Cu(1)—N(9)	82.41(6)
N(1)—Cu(1)—N(9)	99.71(6)
N(7)—Cu(1)—O(6)	81.34(6)
N(1)—Cu(1)—O(6)	96.29(6)
N(9)—Cu(1)—O(6)	162.66(6)
N(7)—Cu(1)—OW1	94.41(6)
N(1)—Cu(1)—OW1	87.91(6)
N(9)—Cu(1)—OW1	89.60(7)
O(6)—Cu(1)—OW1	97.63(6)
N(7)—Cu(1)—OW2	86.10(6)
N(1)—Cu(1)—OW2	91.67(6)
N(9)—Cu(1)—OW2	88.21(7)
O(6)—Cu(1)—OW2	84.69(6)
OW1—Cu(1)—OW2	177.67(5)
C(2)—N(1)—C(5)	106.53(14)
C(2)—N(1)—Cu(1)	129.28(11)
C(5)—N(1)—Cu(1)	124.11(12)
C(2)—N(3)—C(4)	109.3(2)

RESULTS AND DISCUSSION

Description of the structures

The molecular structure of [Cu(gg)(H_2O)(creat)] · 1.5 H_2O (**1**) is shown in Fig. 2. The Cu^{II} ion has approximately square-pyramidal coordination being linked to the chelating atoms N(9) α-amino nitrogen [Cu—N(9) = 2.022(2) Å], N(7) amide nitrogen [Cu—N(7) = 1.907(2) Å] and O(6) carboxyl oxygen [Cu—O(6) = 2.0338(14) Å] of the glycylglycine dianion and N(1) of the creatinine molecule [Cu—N(1) = 2.014(2) Å]. The coordination sphere about the copper is completed by an axial water molecule [Cu—OW(1) = 2.496(2) Å]. A second loosely bound axial water molecule [Cu—OW(2) = 2.907(2) Å] extends qualitatively the coordination geometry to octahedral. Thus, Jahn–Teller distortion results in a 4 + 1 + 1 pseudo-elongated coordination octahedron of the copper complex, with OW(1) and OW(2) occupying the apical positions. Bonding angles (Table 2) support the suggestion of a true bonding interaction between copper and this distant apical OW(2) water molecule, although the coordination sphere of Cu^{II} is best described as square pyramidal.

A slight distortion in the square-pyramidal environment of Cu^{II} is indicated by the observed

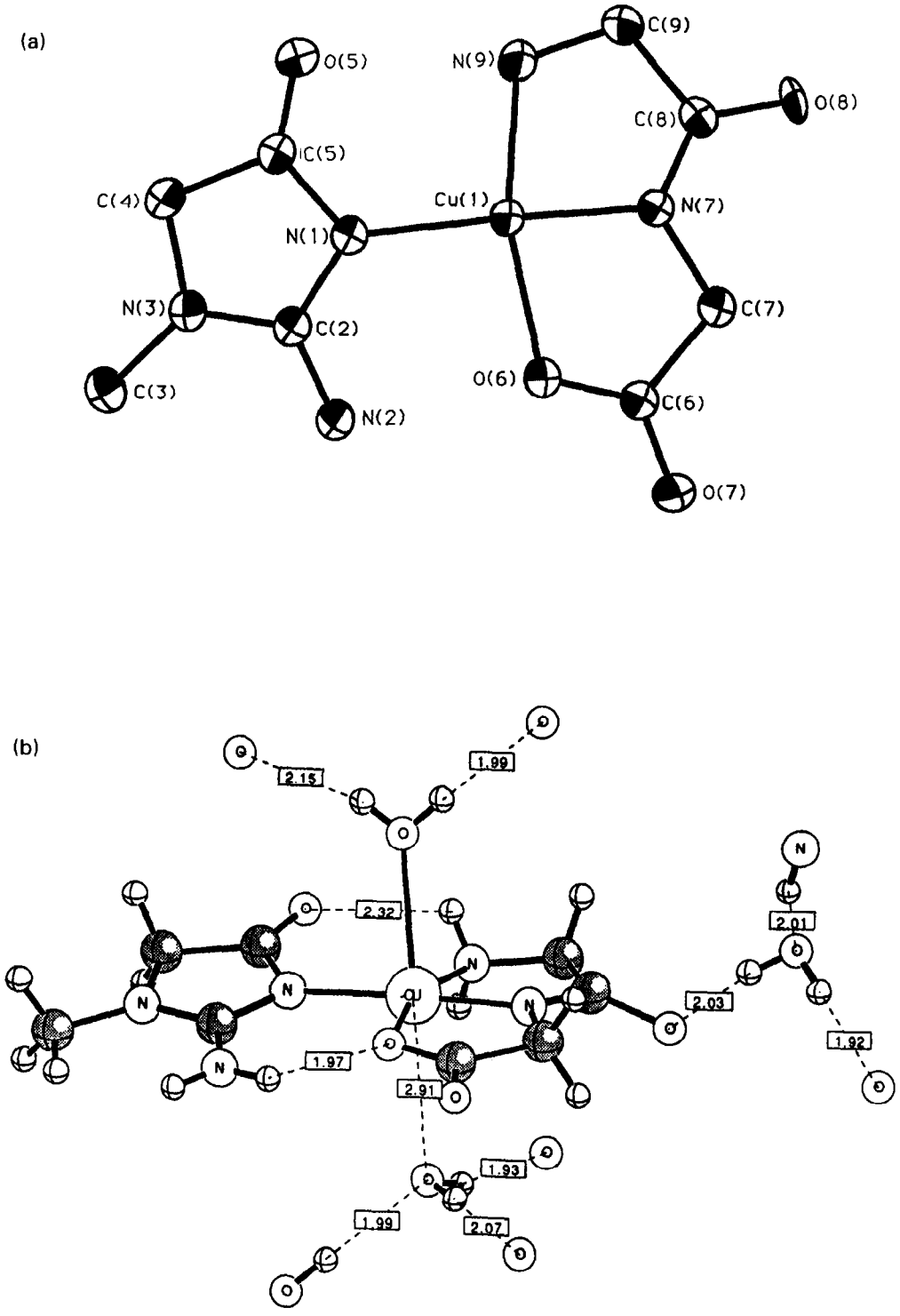

Fig. 2. (a) Molecular structure of the complex without the axial water molecules showing the atom numbering scheme. (b) Crystal structure of $[Cu(gg)(H_2O)(creat)] \cdot 1.5\ H_2O$ (hydrogen atoms included).

bond angles, which vary from 87.91(6) to 97.63(6)°. The copper atom lies somewhat out of the peptide plane [N(9),N(7),O(6)] 0.125 Å and moved towards OW1.

A third non-coordinating disordered water molecule OW(3) with an occupancy factor of 0.5 is located between two complex units [Fig. 3b] interacting with the two disordered O(8A) and O(8B)

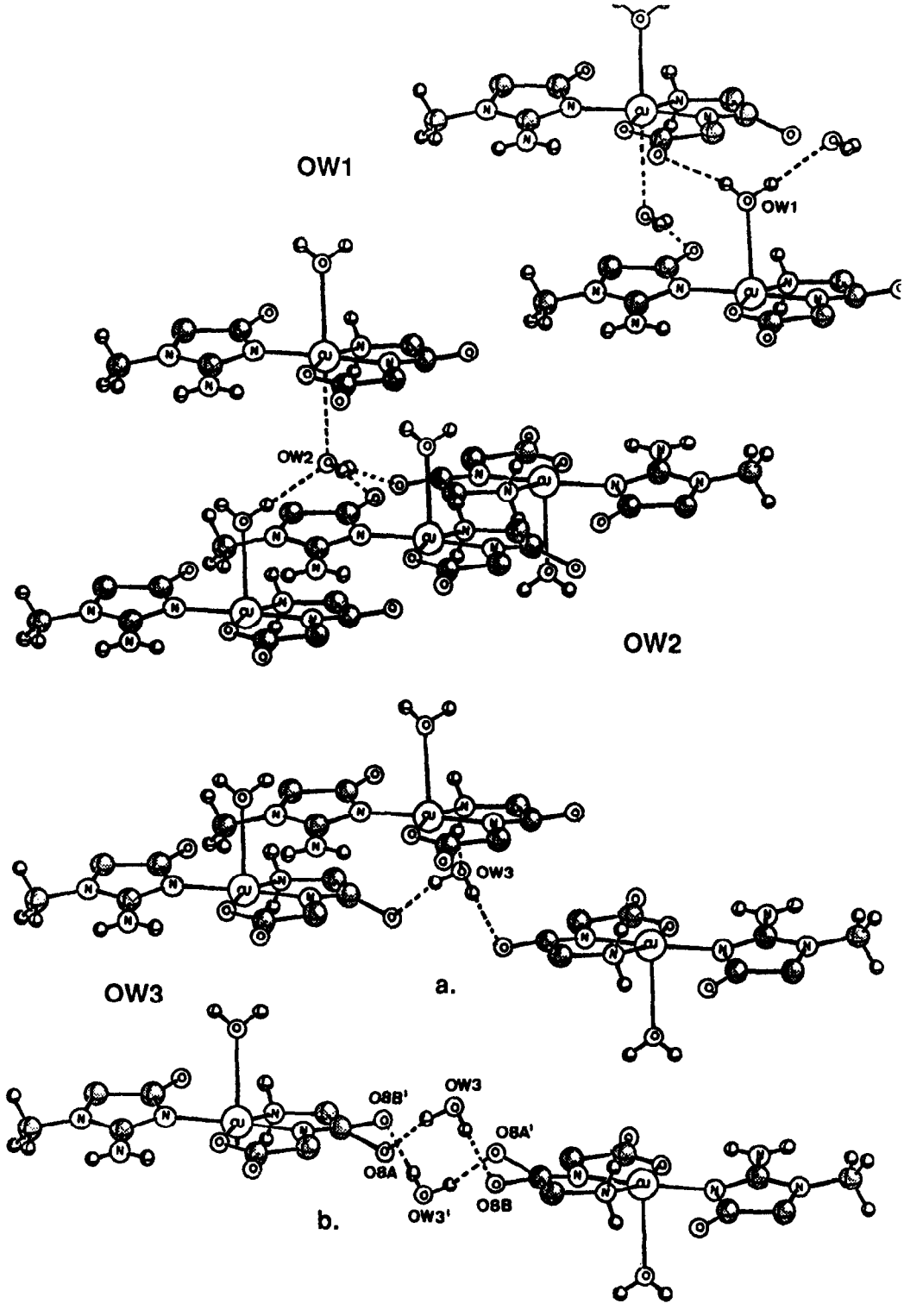

Fig. 3. (a) Packing diagram of the structure of the complex showing the interactions of the three types of water molecules OW1, OW2 and OW3. (b) Drawing of the disordered OW3 water molecule (occupancy factor 0.5).

atoms. There are two equivalent positions for OW3 and only one of them is occupied due to steric factors. Between the two positions there is an inversion centre at (1/2,1,0).

In contrast with other reports[4b,4c] a nearly coplanar arrangement of the creatinine ring and the peptide moiety is observed [torsion angles O(6)—Cu(1)—N(1)—C(2) = −8.95° and N(9)—Cu(1)—N(1)—C(5) = −19.35°]. It is worth noting the existence of two strong intramolecular hydrogen bonds: N(2)—H···O(6) = 1.967 and N(9)—H···O(5) = 2.319 Å, which strongly stabilize this disposition (see Fig. 2).

The bond distances and bond angles within the creatinine molecule are comparable to those obtained earlier for the free base[20] and suggest an extensive π-electron delocalization in the creatinine molecule with the exception of the C(5)—C(4), C(4)—N(3) and N(3)—C(3) bonds.

The glycylglycine dianion has approximately the same chelate angles (Table 2), as observed in other glycylglycinato copper(II) complexes[4c,12b,13] [O(6)—Cu—N(9) = 162.66(6)°, O(6)—Cu—N(7) = 81.34 (6)°, N(9)—Cu—N(7) = 82.41(6)°].

Crystal packing is depicted in Fig. 4. The packing of the complex units is governed by a network of intermolecular hydrogen contacts in which the three types of water molecules take part. All interactions between complex units are observed through water molecules except the strong molecular hydrogen bonds [O7···H_A—N(2) = 2.096 Å]. The OW1 water molecule is bound through strong hydrogen bonds to another water molecule [OW1—H···OW2 = 1.989 Å] and the O(7) of an adjacent complex unit [OW1—H···O(7) = 2.153 Å]. In addition, OW2 interacts with O(8) [OW2—H···O(8A) = 1.934 or OW2—H···O(8B) = 2.054 Å] and the O(5) [OW2—H···O(5) = 2.069 Å] of two symmetrically disposed complex units. Hydrogen-bonding interactions involving the water molecule OW3 maintain strongly held three complex units: OW3—H···O(8A) = 2.031, OW3—H···O(8B) = 1.916 and OW3···H—N(9) = 2.012 Å.

Tables of final atomic coordinates, anisotropic displacement parameters, bond lengths and angles involving hydrogen atoms, least-squares planes, selected torsion angles, and the listing of observed and calculated structural factors are included in the supplementary material.

IR data

The IR spectrum of the ternary compound was recorded down to the far-IR region of 200 cm^{-1} and compared with those of the creatinine ligand and [Cu(gg)$(H_2O)_2$]. Tentative band assignments (cm^{-1}) for creatinine, according to the literature[8a–d,9,21] are: ν(NH)(cyclic)/$\nu_{as}(NH_2)$ = 3256s, br; ν(NH)(imino)/$\nu_s(NH_2)$ = 3040s, br; ν[C(5)=O]+ ν(C=N) = 1692, 1671s, br; ν(C=N) = 1590s, br.

The rather broad character of the NH_2 vibration bands [ν(NH)] at 3408, 3359, 3250–3260 and 3113s, br is suggestive of hydrogen bond participation and the presence of the creatinine ligand in their amino tautomer form.[9b] As occurs in other N(1)-bonded creatinine complexes the νC(5)=O peak is shifted to higher frequencies.[8d,9b,22] The strong band at 1692 cm^{-1} assigned to ν[C(5)=O] in the free creatinine spectrum diminishes in relative intensity, appearing at *ca* 1713 cm^{-1} upon complexation (21 cm^{-1}). Contrarily, in C(5)=O-bonded complexes the ν(C=O) peak is shifted to lower frequencies.[11,23] The bands related to the glycylglycinate copper(II) peptide system at 1624 [ν(C=O)] and 1595 cm^{-1} [$\nu_a(COO^-)$][24] exhibit small shifts in their frequency as a consequence of the new charge distribution and the peaks centred at 1454, 1417, 1374, 1343 and 1297 cm^{-1} remain almost at the same frequency and intensity. The 1580 cm^{-1} band appearing in the spectrum of the complex is assigned to ν(C=N)[8c] of the creatinine moiety with some contribution of the peptide carbonyl broad band (1595 cm^{-1}). Other creatinine bands with ν(C=N) contribution[21b] at 1505, 1419 and 1336 cm^{-1} exhibit intensity changes and little shifts in their frequency. All these data suggest essentially the same bonding scheme of the copper(II)/peptide system and binding between the Cu^{II} and the endocyclic N(1) atom of the creatinine ligand.

Electronic spectra

The electronic spectrum of a 10^{-3} M solution of the complex in methanol has a broad absorption maximum at *ca* 620 nm (ε = 83). The spectrum of the complex in water (10^{-3} M) exhibits a maximum at *ca* 635 nm (ε = 81). Other reported maxima of this broad band are:[25]

Cu(gg)·$3H_2O$	635 nm (ε = 100)	aqueous solution	square-pyramidal
Cu(gg)(dmp)·$5H_2O$	633 nm (ε = 313)	MeOH solution	distorted square-pyramidal
Cu(gg)(bpy)	642 nm (ε = 103)	aqueous solution	distorted square-pyramidal
Cu(gg)(phen)·$3H_2O$	629 nm (ε = 100)	MeOH solution	distorted square-pyramidal
	640 nm (ε = 102)	aqueous solution	

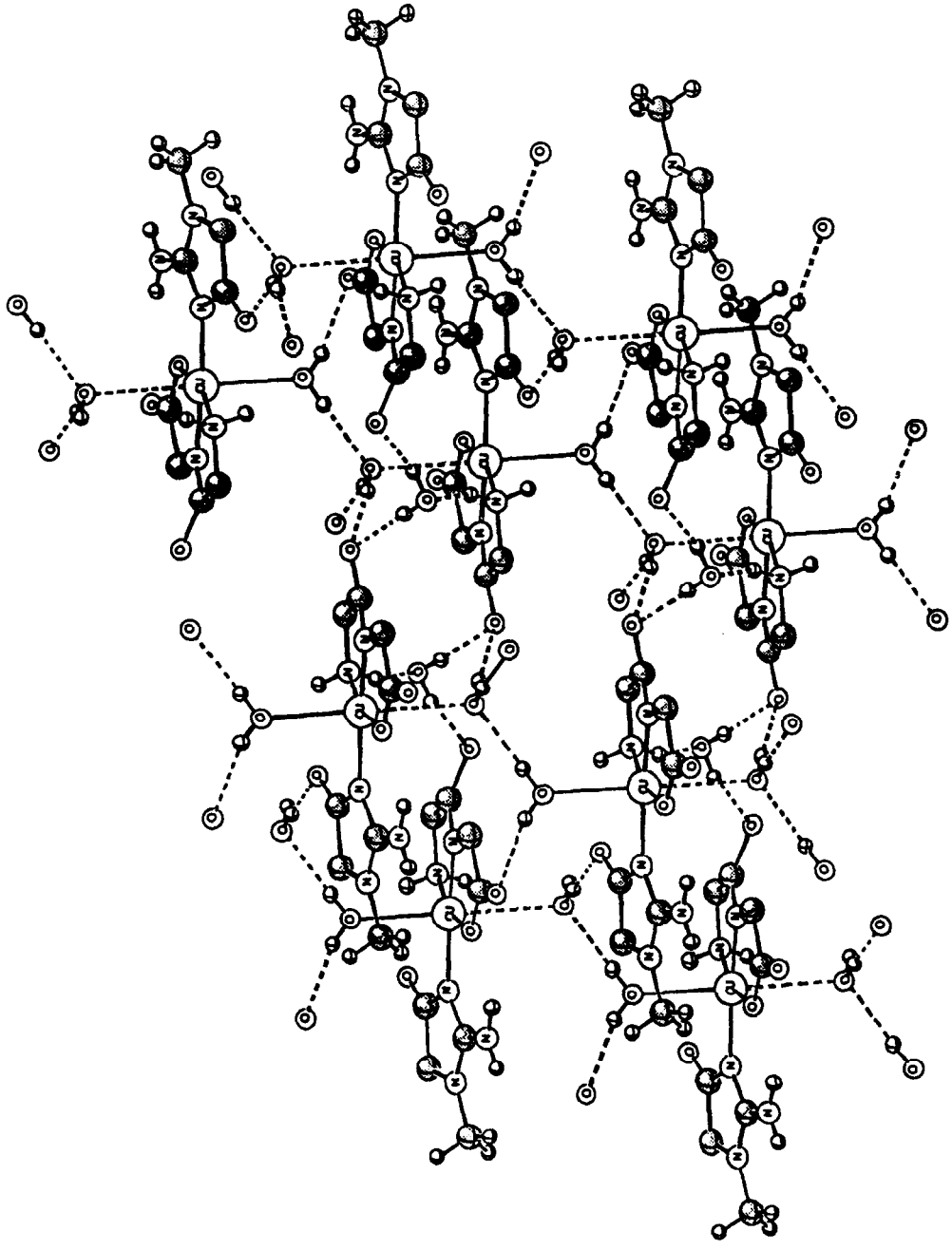

Fig. 4. Stereoview of the complete packing of the ternary complex from an approximate view along c.

These results suggest that the structure found in the crystal persists in solution (MeOH and H_2O at pH = 6) and the *d–d* transition spectrum of the complex is suggestive of approximately square-pyramidal geometry about Cu^{II}. This is consistent with the $\Lambda_M(10^{-3}$ M) values in MeOH (16) and water (31), which implies the presence of non-electrolyte species.[26]

The π–π^* transition band (235 nm, $\varepsilon = 8.08 \times 10^3$) of the creatinine moiety increases its relative intensity appearing at 229 nm ($\varepsilon = 1.31 \times 10^4$) as a shoulder in the spectrum of the complex (methanol) as a consequence of N(1) bonding and subsequent restructuring of the ring charge.

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