Synthesis, Spectroscopic, and Magnetic Studies of Copper(II) with *N*-Protected Amino Acids: Crystal and Molecular Structure of Diaquatetrakis(μ-*N*-benzoyl-α alaninato)-dicopper(II) †

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Eighteen complexes of copper(II) having the general formula $CuL_2{\cdot}nH_2O$ (n = 1—4) with *N*-protected amino acids (HL) have been prepared and characterized by spectroscopic methods and magnetic susceptibility measurements. These complexes belong to three types: binuclear species having bridging bidentate co-ordination through the carboxylate group, mononuclear species having symmetrical chelating bidentate co-ordination or bridging bidentate co-ordination with no Cu–Cu interaction, and mononuclear species having highly unsymmetrical chelating bidentate or non-chelating unidentate co-ordination through the carboxylate group. The complex $[\{Cu(Bz\text{-}\alpha\text{-}AlaO)_2(H_2O)\}_2]$ crystallizes in the triclinic system with space group $P\bar{1}$, and unit-cell parameters a = 9.421(2), b = 9.549(2), c = 12.618(3) Å, α = 74.31(2), β = 79.21(2), γ = 88.69(2)°, and Z = 1. Full-matrix least-squares refinement using 2 842 independent reflections converged to a final R = 0.038 and R' = 0.052. The complex has a typical copper(II) acetate monohydrate type structure with mean Cu–O(carboxylate), Cu–O(water), and Cu–Cu distances of 1.968(3), 2.138(4), and 2.664(1) Å, respectively.

Complexes of amino acids and peptides with metal ions act as models for metal–protein reactions. It has been observed that with simple amino acids, if there is no complicating donor-site chain, co-ordination takes place solely through amino and carboxylate groups, thereby forming five- or six-membered rings. Co-ordination is favoured because of the strongly basic nature of the amino nitrogen and the presence of the carboxyl oxygen which acts as an anchor during formation of a chelate ring with the metal ion. Substitution of the amino nitrogen by groups such as acetyl, benzoyl, or benzyloxycarbonyl decreases the affinity of the amino group for the metal. In such cases, co-ordination takes place only through the carboxylate groups. With Cu^{II} the carboxylate group can act as non-chelating unidentate,[1,2] chelating bidentate,[3] and bridging bidentate.[4,5]

We report the synthesis and investigation of eighteen complexes of copper(II) with *N*-protected amino acids and the *X*-ray crystal-structure determination of diaquatetrakis(μ-*N*-benzoyl-DL-α-alaninato)-dicopper(II).

Experimental

The ligands were synthesized according to procedures already described.[6]

Preparation of the Complexes.—Diaquatetrakis(μ-*N*-benzoyl-α-alaninato)-dicopper(II), $[\{Cu(Bz\text{-}AlaO)_2(H_2O)\}_2]$, was prepared by adding freshly prepared copper hydroxide (*ca.* 0.0012 mol) to a hot solution of the amino acid (0.002 mol) in water–n-propanol (1:3) (25 cm^3) solvent. The reaction mixture was heated on a water-bath for 1 h. The excess of copper hydroxide was separated from the blue solution, and from the filtrate bluish green prism-like crystals appeared after 72 h (yield 80%).

General preparation of copper(II) *complexes with* N-*benzoylamino acids.* Copper(II) complexes with *N*-benzoylamino acids, HL, having the general formula $CuL_2{\cdot}nH_2O$, where n varies from 1 to 4, were prepared by adding freshly prepared copper hydroxide (0.0012 mol) to a hot solution of amine acid (0.002 mol) in water–ethanol (1:3) (25 cm^3) solvent. The reaction mixtures were heated for 1 h and the excess of copper hydroxide was filtered off. The filtrates were concentrated by evaporation in the open and allowed to stand overnight, when green crystals separated out. These were washed with acetone and dried in a vacuum at room temperature.

General preparation of copper(II) *complexes with other* N-*acylamino acids.* Freshly prepared copper hydroxide (*ca.* 0.0012 mol) was added to the hot solution of the amino acid (0.002 mol) in water (25 cm^3) and the reaction mixture was heated for about 1 h. The unreacted copper hydroxide was separated by filtration. The filtrate was evaporated in the open to a semi-solid state and kept in a sulphuric acid desiccator for a few days. The solid formed was powdered and finally dried in a vacuum at room temperature.

Physical Measurements.—Infrared spectra were recorded in the region 4000—200 cm^{-1} on a SP3-300 Philips Scientific spectrophotometer using KBr pellets, u.v. spectra on a VSU2-P Carl Zeiss spectrophotometer. The magnetic suceptibilities of powdered samples of the metal complexes at room temperature were measured by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections for the ligands and metal ions were applied by using appropriate Pascal constants.

Crystallography.—*Crystal data.* $[\{Cu(Bz\text{-}\alpha\text{-}AlaO)_2(H_2O)\}_2]$, $C_{40}H_{44}Cu_2N_4O_{14}$, M = 932, triclinic, a = 9.421(2), b = 9.549(2), c = 12.618(3) Å, α = 74.31(2), β = 79.21(2), γ = 88.69(2)°, U = 1 078.2(4) Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.44 g cm^{-3}, $F(000)$ = 482, graphite-monochromatized Mo-K_α radiation, λ = 0.710 73 Å, μ(Mo-K_α) = 10.5 cm^{-1}.

Measurements were made on a crystal of dimensions 0.25 × 0.20 × 0.20 mm, using a Nicolet R3m/V diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment using setting angles for 15 reflections having $16 < 2\theta < 30°$. Intensities of all independent reflections

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical data[a] (%)

Complex[b]	C	H	N	Cu
(1) $[Cu(Ac\text{-}GlyO)_2]\cdot 4H_2O$[c]	26.95 (26.10)	5.15 (5.45)	8.00 (7.60)	17.35 (17.25)
(2) $[Cu(Ac\text{-}PheO)_2]\cdot H_2O$	54.10 (53.35)	5.35 (5.25)	6.10 (5.65)	12.40 (12.85)
(3) $[Cu(Ac\text{-}LeuO)_2]\cdot H_2O$	44.55 (45.10)	6.25 (7.05)	6.30 (6.60)	15.35 (14.90)
(4) $[Cu(CH_2ClCO\text{-}GlyO)_2]\cdot 4H_2O$	21.60 (22.00)	4.85 (4.10)	7.00 (6.40)	14.10 (14.55)
(5) $[Cu(CH_2ClCO\text{-}AlaO)_2]\cdot H_2O$	30.10 (29.25)	3.10 (3.90)	7.45 (6.30)	15.10 (15.45)
(6) $[Cu(CH_2ClCO\text{-}PheO)_2]\cdot H_2O$	48.10 (46.95)	3.65 (4.25)	5.35 (5.00)	11.65 (11.30)
(7) $[Cu(CH_2ClCO\text{-}LeuO)_2]\cdot H_2O$	39.10 (38.80)	5.20 (5.65)	6.20 (5.65)	12.55 (12.85)
(8) $[Cu(CCl_3CO\text{-}AlaO)_2]\cdot H_2O$[d]	22.60 (21.90)	1.75 (2.20)	5.60 (5.10)	12.00 (11.55)
(9) $[Cu(CF_3CO\text{-}GlyO)_2]\cdot H_2O$[d]	23.25 (22.80)	2.10 (1.90)	6.50 (6.65)	15.15 (15.05)
(10) $[Cu(CF_3CO\text{-}AlaO)_2]\cdot H_2O$[d]	25.90 (26.70)	2.00 (2.20)	6.20 (6.25)	13.85 (14.10)
(11) $[Cu(CF_3CO\text{-}ValO)_2]\cdot H_2O$	34.10 (33.25)	4.15 (3.95)	5.80 (5.25)	12.45 (12.55)
(12) $[Cu(Bz\text{-}GlyO)_2]\cdot H_2O$[c]	48.90 (49.35)	3.70 (4.10)	6.80 (6.40)	14.30 (14.50)
(13) $[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$	51.55 (51.55)	4.50 (4.75)	6.20 (6.00)	13.20 (13.65)
(14) $[Cu(Bz\text{-}ValO)_2]\cdot H_2O$	54.80 (55.20)	5.35 (5.75)	5.65 (5.35)	13.00 (12.20)
(15) $[Cu(Bz\text{-}LeuO)_2]\cdot H_2O$	56.95 (56.80)	6.80 (6.20)	5.80 (5.10)	11.30 (11.55)
(16) $[Cu(HCO\text{-}PheO)_2]\cdot 2H_2O$	49.15 (49.65)	4.75 (5.00)	6.05 (5.80)	13.45 (13.15)
(17) $[Cu(HCO\text{-}ValO)_2]\cdot 2H_2O$	36.55 (37.16)	5.60 (6.20)	7.80 (7.20)	16.70 (16.40)
(18) $[Cu(HCO\text{-}LeuO)_2]\cdot 2H_2O$	41.70 (42.25)	5.90 (6.55)	7.55 (7.05)	15.70 (15.95)

[a] Calculated values are given in parentheses. [b] Abbreviations for the amino acid ligands are in accord with the I.U.P.A.C.–I.U.B. (*Pure Appl. Chem.*, 1984, **56**, 595). [c] Included for reference purposes only. [d] Slightly hygroscopic.

Table 2. Electronic and i.r. spectra (cm^{-1})

Complex	$\mu_{eff.}$	Reflectance	ν(NH)	δ(NH)	ν(CO)	ν(OCO)		Δν	Type of complex
						asym	sym		
(3)	1.54	26 570, 13 160	3 340s, 3 430	1 555m	1 645(sh)	1 612vs	1 418s	194	I
(4)	2.01	27 030, 12 990	3 360sbr	1 545s	1 675s	1 640vs	1 415	225	I
(5)	1.70	26 670(sh), 13 510	3 410vs	1 540s	1 645(sh)	1 625vs	1 420s	205	I
(7)	1.85	26 320(sh), 12 500	3 400s, 3 330s	1 550s	1 652(sh)	1 625vs	1 415s	210	I
(13)	1.52	26 320, 12 700	3 400s, 3 430s		1 665(sh)	1 635vs	1 425vs	210	I
(14)	1.52	26 320, 14 710	3 310m, 3 340m	1 530s	1 645s	1 600vs	1 420s	180	I
(15)	1.75	27 030, 13 700	3 440s	1 520s	1 640s	1 612vs	1 415s	197	I
(17)	1.76	13 510	3 250s		1 660(sh)	1 650vs	1 425s	225	II
(2)	1.58	13 510, 12 345(sh)	3 350s, 3 400s	1 542s	1 645s	1 597s	1 420s	177	II
(6)	1.92	13 070	3 310sbr, 3 400sbr	1 542s	1 650(sh)	1 620vs	1 415vs	205	II
(9)	2.22	12 660	3 300s, 3 230s		1 690vs	1 635vs	1 420s	215	II
(8)	2.20	13 980	3 310sbr, 3 400sbr	1 510s	1 695(sh)	1 590vs	1 420s	170	II
(10)	2.22	12 820	3 440sbr		1 685vs	1 595vs	1 435s	160	II
(12)	2.03	13 150	3 420s	1 550s		1 630vs	1 420s	210	II
(1)	2.02	15 200, 12 800	3 310vs, 3 420s	1 562s		1 610vs	1 395s	215	III
(11)	2.07	14 200	3 450s	1 545(sh)	1 720vs	1 605vs	1 395m	210	III
(16)	2.08	13 160, 13 160	3 250s, 3 340s		1 660(sh)	1 630vs	1 385s	245	III
(18)	1.99	13 300	3 260s		1 670(sh)	1 625vs	1 390s	235	III

with $3.5 < 2\theta < 45.0°$ were measured in θ—2θ scan mode using a variable scan speed between 3.98 and 29.30° min^{-1}. Of 3 244 (2 842 independent) reflections measured, 2 289 with $I > 3\sigma(I)$ were taken as observed. The stability of the crystal was checked by measuring two standard reflections every 50 reflections. The data were corrected for Lorentz, polarization, and absorption effects.

The structure was solved by direct methods[7] followed by full-matrix least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms. All hydrogen atoms, except the two attached to the water molecule, were calculated geometrically at idealized positions with C–H 0.96 Å. All H atoms were allotted an U_{iso} value of 0.060 $Å^3$. The refinement for 278 parameters converged to a final $R = 0.038$ and $R' = 0.052$, minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0.008\ 29F_o^2]$. The final difference map was featureless. Complex neutral atom scattering factors[8] were used in all the calculations. The dihedral angles, least-squares planes, and hydrogen bonding were calculated using the computer program PARST.[9]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

All the complexes correspond to the general formula $CuL_2{\cdot}nH_2O$, where n ranges from 1 to 4 (Table 1). Their i.r. spectra were compared with those of the respective amino acids and their sodium salts. Either no shift or a shift to higher frequency of the N–H stretching vibration, amide (II) and amide (I) bands, excludes co-ordination from the NH or CO group. In the copper(II) complexes with trifluoroacetyl derivatives of amino acids the small shift of the CO band to lower frequencies may be due to stronger hydrogen bonding in the complexes or its co-ordination to the metal ion. The magnetic moments of the complexes (Table 2) were measured only at room temperature. On the basis of the modes of co-ordination by the carboxylate group these complexes can be classified into three types.

Table 3. Atomic co-ordinates (× 10^4) for [{Cu(Bz-α-AlaO)$_2$(H_2O)}$_2$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	−263(1)	−278(1)	−925(1)	C(10)	−4 994(6)	−2 103(6)	5 206(4)
O(W)	−993(3)	−504(3)	−2 377(3)	O(4)	501(4)	−2 195(3)	−351(3)
O(1)	−2 146(3)	−878(4)	68(3)	C(11)	888(5)	−2 544(5)	583(4)
C(1)	−2 504(5)	−854(5)	1 063(4)	O(5)	866(3)	−1 758(3)	1 225(2)
O(2)	−1 725(3)	−433(3)	1 633(2)	C(12)	1 415(7)	−4 062(5)	955(4)
C(2)	−4 039(6)	−1 388(8)	1 600(4)	C(13)	2 737(10)	−4 274(9)	152(5)
C(3)	−4 250(9)	−2 986(9)	1 487(7)	N(2)	1 646(4)	−4 383(4)	2 101(3)
N(1)	−4 373(4)	−1 403(5)	2 776(3)	C(14)	1 600(6)	−5 721(5)	2 758(4)
C(4)	−5 732(5)	−1 388(5)	3 313(4)	O(6)	1 512(7)	−6 743(4)	2 365(4)
O(3)	−6 753(3)	−1 348(4)	2 818(3)	C(15)	1 646(5)	−5 929(5)	3 960(4)
C(5)	−5 981(5)	−1 552(5)	4 544(4)	C(16)	1 093(6)	−7 247(5)	4 720(5)
C(6)	−7 318(6)	−1 159(6)	5 040(4)	C(17)	1 035(6)	−7 478(6)	5 845(5)
C(7)	−7 626(7)	−1 332(6)	6 188(5)	C(18)	1 529(6)	−6 429(7)	6 245(4)
C(8)	−6 639(7)	−1 895(7)	6 824(5)	C(19)	2 110(7)	−5 145(6)	5 513(4)
C(9)	−5 315(7)	−2 275(7)	6 343(4)	C(20)	2 148(6)	−4 899(5)	4 379(4)

Type (I) *Complexes.*—The diffuse reflectance spectrum of this type of complex has one main band in the range 12 500—14 710 cm^{-1} and a shoulder in the range 26 320—27 030 cm^{-1} (Table 2). The first band is due to *d–d* transitions and second is a shoulder considered to be diagnostic of a dimeric structure.[10] The ν_{sym}(OCO) is in the range 1 415—1 425 cm^{-1} which according to the reported criterion[11] indicates bridging bidentate co-ordination of the carboxylate group. The subnormal magnetic moments of these complexes support a copper(II) acetate monohydrate type structure.

Type (II) *Complexes.*—All these complexes have one broad band in the diffuse reflectance spectra, centred in the range 12 660—13 980 cm^{-1}; [Cu(Ac-PheO)$_2$]·H_2O has an additional shoulder at 12 345 cm^{-1}. These bands are consistent with a CuO_{4-6} chromophore.[12] Absence of a band in the range 26 000—27 000 cm^{-1} indicates the monomeric nature of these complexes. The ν_{sym}(OCO) in the range 1 415—1 435 cm^{-1} indicates bidentate co-ordination of the carboxylate group. The $\mu_{eff.}$ values of all the complexes lie in the range 1.76—2.22, except for [Cu(Ac-PheO)$_2$]·H_2O. The higher $\mu_{eff.}$ values suggest the absence of copper(II)–copper(II) interaction. All these complexes are therefore mononuclear species having symmetrical chelating bidentate co-ordination or bridging bidentate co-ordination with no copper copper interaction.

Type (III) *Complexes.*—For these complexes ν_{sym}(OCO) lies in the range 1 385—1 395 cm^{-1} (Table 2), always to lower energy compared to that of the corresponding sodium salt. These facts support chelating bidentate co-ordination of the carboxylate group.[11] However, according to the band-shift criterion, the shift of ν_{asym}(OCO) to higher frequency and that of ν_{sym}(OCO) to lower frequency, as compared to their respective positions for the sodium salts, indicates unidentate co-ordination of the carboxylate group, which is further supported by Δν of the copper(II) complexes being greater than of the corresponding sodium salts. Hence a highly unsymmetrical bidentate chelation can be proposed for these complexes where unidentate co-ordination is the limiting case. The magnetic moment values suggest a mononuclear structure, supported by the absence of any band in the range 26 000—27 000 cm^{-1} in the reflectance spectra. Broad bands in the region 13 160—14 200 cm^{-1}, except in the case of [Cu(Ac-GlyO)$_2$]·4H_2O, are consistent with the presence of a CuO_{4-6} chromophore. The complex [Cu(Ac-GlyO)$_2$]·4H_2O has an absorption band at 15 200 cm^{-1} with a pronounced shoulder at 12 800 cm^{-1} which indicates a stronger tetragonal distortion, leading to essentially a square-planar stereochemistry as confirmed by the reported crystal structure.[3]

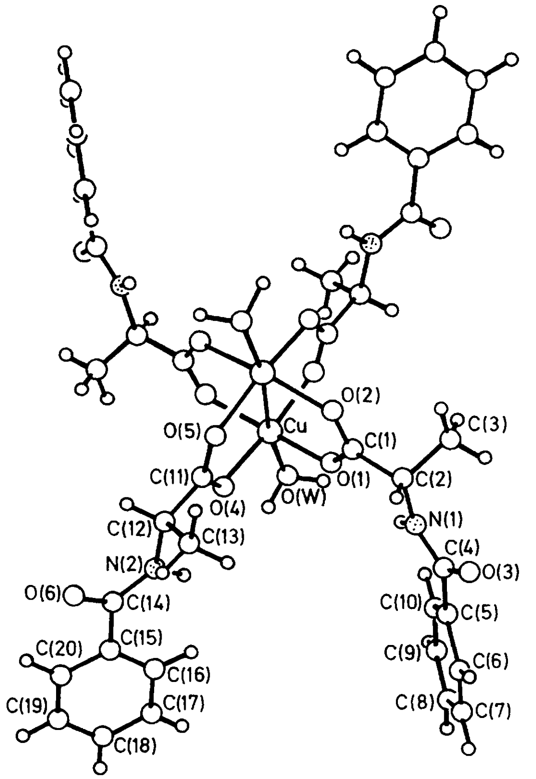

Figure. Perspective view of the molecule [{Cu(Bz-α-AlaO)$_2$(H_2O)}$_2$] showing the atom labelling scheme. Unlabelled atoms are related to the labelled ones through a centre of symmetry

Description of Structure of [{Cu(Bz-α-AlaO)$_2$(H_2O)}$_2$].—The crystal structure of this complex consists of centrosymmetric dimeric units in which two copper ions are bridged by four carboxylate groups (Figure). The co-ordination around each copper(II) ion is approximately square pyramidal. Four oxygen atoms at the equatorial positions are almost planar with copper(II) being 0.21 Å above this plane. A water molecule occupies an axial position. A distorted octahedron is completed by another copper(II) at 2.664 Å, as found in the structure of classic dimeric copper(II) acetate monohydrate.[13,14] The

Table 4. Bond lengths (Å) and angles (°)* for $[\{Cu(Bz\text{-}\alpha\text{-}AlaO)_2(H_2O)\}_2]$

Cu–O(W)	2.138(4)	N(1)–C(4)	1.333(6)
Cu–O(1)	1.968(3)	C(4)–O(3)	1.236(6)
Cu–O(2′)	1.968(3)	C(4)–C(5)	1.492(6)
Cu–O(4)	1.959(3)	O(4)–C(11)	1.256(6)
Cu–O(5′)	1.978(3)	C(11)–O(5)	1.244(6)
Cu–Cu′	2.664(1)	C(11)–C(12)	1.508(6)
O(1)–C(1)	1.244(6)	C(12)–C(13)	1.499(10)
C(1)–O(2)	1.259(6)	C(12)–N(2)	1.451(6)
C(1)–C(2)	1.514(7)	N(2)–C(14)	1.323(5)
C(2)–C(3)	1.598(12)	C(14)–O(6)	1.224(7)
C(2)–N(1)	1.455(7)	C(14)–C(15)	1.483(7)
O(W)–Cu–O(1)	93.7(1)	O(W)–Cu–O(5′)	91.0(1)
O(W)–Cu–O(4)	102.0(1)	O(1)–Cu–O(5′)	89.3(1)
O(1)–Cu–O(4)	90.8(1)	O(4)–Cu–O(5′)	167.0(2)
O(W)–Cu–Cu′	170.4(1)	Cu′–Cu–O(5′)	81.4(1)
O(1)–Cu–Cu′	80.5(1)	O(2)–Cu–O(5′)	88.5(1)
O(4)–Cu–Cu′	85.8(1)	Cu–O(1)–C(1)	127.1(3)
O(W)–Cu–O(2′)	98.7(1)	O(1)–C(1)–O(2)	126.4(4)
O(1)–Cu–O(2′)	167.4(1)	O(1)–C(1)–C(2)	114.4(5)
O(4)–Cu–O(2′)	88.7(1)	O(2)–C(1)–C(2)	119.2(4)
Cu′–Cu–O(2′)	87.0(1)	C(1)–O(2)–Cu′	119.0(3)
C(1)–C(2)–C(3)	108.9(5)	O(5)–C(11)–C(12)	117.6(4)
C(1)–C(2)–N(1)	111.9(5)	C(11)–O(5)–Cu′	125.6(3)
C(3)–C(2)–N(1)	109.6(5)	C(11)–C(12)–C(13)	110.3(4)
C(2)–N(1)–C(4)	121.6(4)	C(11)–C(12)–N(2)	110.6(4)
N(1)–C(4)–O(3)	120.7(4)	C(13)–C(12)–N(2)	112.8(5)
N(1)–C(4)–C(5)	117.8(4)	C(12)–N(2)–C(14)	122.5(4)
O(3)–C(4)–C(5)	121.3(4)	N(2)–C(14)–O(6)	119.5(5)
Cu–O(4)–C(11)	121.0(3)	N(2)–C(14)–C(15)	118.4(5)
O(4)–C(11)–O(5)	126.0(4)	O(6)–C(14)–C(15)	122.1(4)
O(4)–C(11)–C(12)	116.4(4)		

* Bond distances and angles involving phenyl rings have been excluded.

peptide groups are not involved in bonding. The fractional co-ordinates are given in Table 3 and bond distances and angles in Table 4. The Cu–O(carboxyl) bond lengths are in full agreement with those found for $[\{Cu(Ac\text{-}GlyO)_2(H_2O)\}_2]$[4] and $[\{Cu(Ac\text{-}\beta\text{-}AlaO)_2(H_2O)\}_2]$.[5] The mean Cu–O(carboxyl) bond length [1.968(3) Å] is in good agreement with the value of 1.97 Å given by Freeman[15] for the Cu^{II}–O(carboxyl) bond in amino acid complexes and is in the range 1.89—2.02 Å found in many copper(II) carboxylates.[16]

The Cu–Cu separation (2.664 Å) in this complex is greater than that (2.556 Å) found in metallic copper[17] and 2.544 Å in polymeric copper(I) acetate,[18] but is comparable to 2.616—2.645 Å found in several dimeric copper(II) carboxylates.[19] This distance agrees well with that found in $[\{Cu(Ac\text{-}GlyO)_2(H_2O)\}_2]$ and $[\{Cu(Ac\text{-}\beta\text{-}AlaO)_2(H_2O)\}_2]$ and indicates that there is a fairly strong Cu–Cu interaction in the complex. The Cu–O(1)–C(1)–O(2)–Cu′ and Cu–O(4)–C(11)–O(5)–Cu′ bridge lengths of 6.435 and 7.437 Å agree well with those found in analogous complexes† and are within the range 6.41—6.46 Å found in several copper(II) carboxylates.

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† Prime represents the centrosymmetric atom.

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