Investigation on coordination ability of N-chloro-acetylglycine towards Cu(II) in solid and solution state

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Abstract

The solution and solid state behavior of the binary system Cu(II)-N-chloroacetylglycine (Cl-acglyH) and the corresponding ternary systems with 2,2'-bipyridine (bpy) and 1,10-phenanthroline (ophen) were investigated by means of pH-metric and spectrophotometric titrations. The X-ray crystal structure of the complex [Cu(ophen)(Cl-acgly)$_2$] · 2H$_2$O (Cl-acgly = N-chloroacetylglycine monoanion) is also reported. The crystals of the compound C$_{20}$Cl$_2$CuN$_4$O$_8$H$_{22}$ are monoclinic, space group $P2_1/c$, $a = 17.574(3)$, $b = 7.125(2)$, $c = 25.113(6)$ Å, $\beta = 130.04(2)°$, $Z = 4$, $R = 0.077$, $R_w = 0.088$. The structure consists of monomeric [Cu(ophen)(Clgly)$_2$] units and lattice water molecules. The Cu(II) atom is square planar coordinated by two carboxylic oxygens of two amino acid molecules and two nitrogen atoms of the ophen molecule. Two long contacts involve the uncoordinated carboxylic oxygens. Crystal packing is due to ring-stacking interaction involving ophen molecules and to a strong intramolecular hydrogen bond involving the chlorine atom and the amidic nitrogen of one ligand molecule. In solution the species [CuL$_2$] and [CuALOH] (A = bpy or ophen) prevail in the binary and ternary system, respectively, both arising from carboxylic-oxygen–metal coordination of the amino acid molecule. The coordination of the OH$^-$ group in the ternary species prevents metal hydrolysis up to pH 11. The possibility of forming hydrogen bond interactions involving the chlorine atom seems the to be determinant factor in stabilizing the ternary complexes. © 1998 Elsevier Science S.A.

1. Introduction

The N-protected amino acids, where the protecting group is an acetyl or benzoyl group, represent the simpler systems in which one peptide linkage is present and have always been found to coordinate the copper(II) ion via the carboxylate group. In aqueous solution the interaction of N-acetyl- and N-benzoylglycine with metal ions such as Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} leads to the formation of very weak carboxylate complex species. In any case, no sign of amide hydrogen deprotonation is ever observed before metal(II) hydroxide precipitation. The only metal ions active in the substitution of amide hydrogen are Pd^{2+} and Pb^{2+}, which, in aqueous solution with N-benzoylglycine, form stable complex species where the amino acid acts as bidentate chelate via carboxylic oxygen and deprotonated amide nitrogen.

In the solid state, the structure of bis(N-acetylglycinato)diaquocopper(II)dihydrate [1,2] consists of monomeric units in which the copper(II) atom is coordinated by two centrosymmetrically related carboxylic oxygens and two water molecules in an essentially square-planar arrangement; the short Cu···O(2) interaction of 2.614(3) Å involving the second carboxylate oxygen is not sufficient to assign a tetragonal geometry, since the angle between the Cu···O(2) vector and the normal to the coordination plane, whose value is 36.4°, prevents the overlap of the metal–ligand orbitals. In a few anhydrous complexes a second metal binding site of such N-protected amino acids is found to be the carbonyl oxygen, which is more basic than the amide nitrogen. In catena-poly{ [μ-(N-acetyl)-❋●valinato)-O^1:O^3]-copper(II) } [3] the ligand bridges two different copper(II) ions via one carboxylic oxygen and the carbonylic oxygen atom, giving rise to a polymeric network of square-planar CuO$_4$ arrangements. Nevertheless, in the [Cu(ophen)(hyda)$_2$] · H$_2$O [4] the participation of the terminal NH$_2$ group in the resonance of the

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amide group in hydantoic acid enhances the basicity of the amidic nitrogen, making it an alternative to carboxylic oxygen as a second active binding site.

The addition of a second ligand molecule, such as 2,2'-bipyridine or 1,10-phenanthroline, leads to a slight tetrahedral distortion in the square-planar arrangement of the copper(II) ion (cis-CuO$_2$N$_2$ chromophore) or to tetragonally elongated square-pyramidal geometry (cis-CuO$_3$N$_2$ chromophore) [5], while in aqueous solution, the stability of ternary complexes prevents the precipitation of the metal hydroxide even at pH > 11 [6].

Here we report a solution and solid-state investigation into Cu(II)-N-chloroacetylglycine and its ternary 2,2'-bipyridine and 1,10-phenanthroline containing systems in order to verify the effect of the chlorine-substituted methyl on the coordination behavior of N-acetylglycine. The crystal and molecular structure of the [Cu(ophen)(Cl-acgly)$_2$] · 2H$_2$O complex is also discussed.

2. Experimental

N-chloroacetyl glycine (Cl-acglyH) was purchased from Sigma and used as received.

2.1. Preparation of the complexes

Cu(Cl-acgly)$_2$ · 2H$_2$O (Cl-acgly = N-chloroacetylglycine monoanion) was prepared by adding 0.02 dm^3 of an aqueous solution (0.05 mol dm^{-3}) of copper(II) acetate monohydrate to 0.02 dm^3 of an aqueous solution of the amino acid (0.1 mol dm^{-3}). A crystalline blue complex separated from a very concentrated solution (0.01 dm^3). Anal. Found: C, 23.9; H, 3.5; N, 6.9. Calc. for C$_8$Cl$_2$H$_{14}$CuN$_2$O$_8$: C, 24.0; H, 3.5; N, 7.0%. Yield: 60%.

Cu(A)(Cl-acgly)$_2$ · 2H$_2$O (A = bpy or ophen). These compounds were prepared by dissolving 0.5 mmol of the binary complex in 0.03 dm^3 of hot water and mixing in 0.010 dm^3 of a methanolic solution (0.05 mol dm^{-3}) of bpy or ophen. Blue crystalline compounds separated after slow evaporation of the solution. Cu(bpy)(Cl-acgly) · 2H$_2$O: Anal. Found: C, 39.7; H, 3.9; N, 9.3. Calc. for C$_{18}$Cl$_2$H$_{20}$CuN$_4$O$_8$: C, 38.8; H, 3.9; N, 10.1%. Yield: 40%.

Cu(ophen)(Clgly) · 2H$_2$O: Anal. Found: C, 41.7; H, 3.5; N, 9.5. Calc. for: C$_{20}$Cl$_2$H$_{22}$CuN$_4$O$_8$: C, 41.3; H, 3.8; N, 9.6%. Yield: 30%.

2.2. Physical measurements

The diffuse reflectance electronic spectra on microcrystalline complexes were obtained with a Perkin-Elmer Lambda 19 spectrophotometer, and IR spectra, using KBr pellets (4000–400 cm^{-1}), with a Brucker Fourier transform IR 113v spectrometer. Carbon, nitrogen, and hydrogen were determined with a C. Erba model 1106 elemental analyzer. The spectrophotometric titrations were performed with a Per-

kin-Elmer Lambda 19 spectrophotometer (cell length 1 cm) in the 1000–500 nm spectral range on solutions containing 0.01 mol dm^{-3} Cu^{2+}, in a Cu:L molar ratio of 1:2, and Cu:A:L (A = bpy or ophen) in a molar ratio of 1:1:2. The pH of the samples was changed using known amounts of concentrated NaOH.

2.3. Crystal data and structure determination

Crystal data, details of data collection and structure-refinement parameters for [Cu(ophen)(Cl-acgly)$_2$] · 2H$_2$O are reported in Table 1. All data were collected at room temperature on an Enraf-Nonius Cad4 diffractometer using graphite-monochromated Mo Kα radiation. The unit cell was determined from 25 well-centered reflections. The intensity data were collected in the ω–2θ scan mode. A total of 4232 reflections were measured to a $\theta_{max} = 25°$; 1559 reflections with $I > 2\sigma(I)$ were used in the refinements. The high number of unobserved reflections was due to the poor quality of the crystal. All attempt to crystallize better crystals were useless. Data reduction including correction for background and Lorentz-polarization effects. An absorption correction was applied according to Ref. [7]. The intensities of two reflections were measured every hour during data collection as a stability check of the diffractometer and of the crystal; no appreciable decay in intensities was observed. The crystal orientation was checked every 200 intensity measurements using two control reflections.

Table 1
Crystal data

| Formula	C$_{20}$Cl$_2$H$_{22}$CuN$_4$O$_8$
Molecular weight	580.9
Space group	$P2_1/c$
a (Å)	17.574(3)
b (Å)	7.125(2)
c (Å)	25.113(6)
β (°)	130.04(2)
V (Å^3)	2407(1)
Z	4
D_{calc} (g cm^{-3})	1.60
D_{obs} (by flotation)	1.58
$F(000)$	1188
Crystal size (mm)	0.21 × 0.35 × 0.55
Radiation, λ (Å)	Mo Kα 0.71069
T (°C)	25
μ (cm^{-1})	11.8
Scan speed (° min^{-1})	2–7
Scan width (°)	1.2 + 0.34 tan θ
θ range (°)	1–25
h range	−20 to 20
k range	0–8
l range	0–29
Scan mode	ω–2θ
Measured reflections	4232
No. reflections used in refinement ($I > 2\sigma(I)$)	1559
$R = \Sigma|\Delta F|/\Sigma|F_o|$	0.077
$R_w = [\Sigma w(\Delta F)^2/\Sigma F_o^2]^{1/2}$	0.088

The structure was solved by direct methods using MUL-TAN [8]. The analysis of the E-map derived from the set of phases with the best combined figure of merit revealed most of the non-hydrogen atoms. The remainder were located from succeeding Fourier syntheses. The structure was aniso-tropically refined by full-matrix least-squares to an R value of 0.077 ($R_w = 0.088$). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1$ for all the observed [$I >$ $2\sigma(I)$] reflections. Hydrogen atoms, included in the structural model in stereochemically calculated positions, were not refined.

Atomic scattering factors and the anomalous dispersion correction were taken from Ref. [9]. All computations were performed using the MOLEN [10] package running on a DEC VAX 6510 computer. The final fractional coordinates are reported in Table 2.

2.4. Potentiometry

$Cu(NO_3)_2 \cdot 3H_2O$ of analytical grade was from C. Erba and standardized with EDTA. Solutions of bpy and ophen (0.005 mol dm^{-3}) (C. Erba) were standardized potentio-metrically with 0.1 mol dm^{-3} HNO$_3$. The NaOH solution (C. Erba) was standardized with potassium hydrogen phthalate (N.B.S.). Potentiometric measurements were performed at $25 \pm 0.1°C$, with a fully automatic ORION 960 autochemistry system, using an ORION 8103SC combined ROSS electrode. All titrations were carried out at constant ionic strength (0.1 mol dm^{-3}) adjusted with solid NaNO$_3$. The standard electrode potential $E°$ was determined before and after each experiment by titration of a known amount of HNO$_3$ (0.1 mol dm^{-3}) with standard NaOH. The ionic product K_w was calculated in the alkaline region of each calibration curve. All experiments were carried out under a nitrogen atmosphere, the equivalent point being determined by the first derivative technique with constant cm^3 increments. The Cu(II):Cl-acglyH binary system was investigated in the 1:4, 1:6 and 1:8 molar ratios with N-chloroacetylglycine concentration ranging from 2.5×10^{-3} to 8×10^{-3} mol dm^{-3}. In all, 80 data were processed. In the ternary systems the Cu(II) concentration was 1×10^{-3} mol dm^{-3} and the Cu/A/Cl-acglyH molar ratios were 1:1:4, 1:1:6 and 1:1:8. For A = bpy and A = ophen respectively, 330 and 256 data were processed. The stability constants were obtained using the SUPERQUAD program [11]. During the refinement $\sigma_e = 0.2$ (mV error) and $\sigma_v = 0.01$ (volume error) were taken into account.

The protonation and stability constants β_{pqrs} are defined as follows:

$$p\text{M} + q\text{A} + r\text{L} + s\text{H} \rightleftharpoons \text{M}_p\text{A}_q\text{L}_r\text{H}_s$$
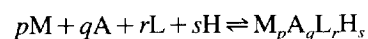
$$\beta_{pqrs} = [\text{M}_p\text{A}_q\text{L}_r\text{H}_s] / [\text{M}]^p[\text{A}]^q[\text{L}]^r[\text{H}]^s$$

where M = metal, L = Cl-acgly, A = bpy or ophen.

Table 2
Final positional parameters and B_{eq} [a]

Atom	x/a	y/b	z/c	B_{eq}
Cu	0.7291(1)	0.0357(3)	0.40805(7)	2.46(3)
O(1A)	0.7957(5)	0.033(2)	0.5064(4)	3.2(2)
O(2A)	0.7777(7)	−0.273(2)	0.4862(5)	5.1(4)
C(1A)	0.8057(8)	−0.137(3)	0.5264(5)	3.6(4)
C(2A)	0.857(1)	−0.176(2)	0.6018(7)	4.3(5)
N(A)	0.8662(7)	−0.010(2)	0.6406(4)	3.5(3)
C(3A)	0.7890(8)	0.046(3)	0.6334(6)	4.4(4)
O(3A)	0.7083(6)	−0.027(3)	0.5977(5)	8.4(5)
C(4A)	0.806(1)	0.219(3)	0.6754(8)	5.4(5)
Cl(A)	0.9159(4)	0.344(1)	0.7119(3)	9.3(2)
O(1B)	0.8513(5)	0.041(2)	0.4220(4)	3.1(2)
O(2B)	0.8524(6)	0.338(2)	0.4474(4)	3.7(3)
C(1B)	0.8856(9)	0.210(2)	0.4376(6)	2.9(4)
C(2B)	0.9783(9)	0.228(2)	0.4420(6)	3.2(4)
N(B)	0.9967(6)	0.420(2)	0.4345(4)	2.7(3)
C(3B)	0.9318(8)	0.505(3)	0.3726(6)	3.5(4)
O(3B)	0.8603(6)	0.424(2)	0.3209(4)	4.3(3)
C(4B)	0.956(1)	0.711(3)	0.3769(8)	5.6(6)
Cl(B)	0.8922(3)	0.8101(9)	0.2947(2)	6.8(1)
N(1)	0.6484(6)	0.038(2)	0.3045(5)	3.5(3)
N(2)	0.5923(6)	0.037(2)	0.3787(5)	3.3(3)
C(1)	0.6803(9)	0.039(3)	0.2691(5)	3.8(4)
C(2)	0.614(1)	0.037(3)	0.1967(6)	5.0(5)
C(3)	0.514(1)	0.033(3)	0.1611(7)	5.1(5)
C(4)	0.4779(8)	0.033(2)	0.1967(6)	3.0(4)
C(5)	0.5498(8)	0.034(2)	0.2699(5)	2.6(3)
C(6)	0.3759(9)	0.029(3)	0.1644(6)	4.2(4)
C(7)	0.3474(9)	0.030(3)	0.2029(7)	5.0(5)
C(8)	0.4191(9)	0.032(3)	0.2779(7)	3.8(4)
C(9)	0.5188(8)	0.037(2)	0.3097(6)	2.7(3)
C(10)	0.3930(8)	0.037(3)	0.3201(7)	4.6(4)
C(11)	0.4671(9)	0.035(3)	0.3896(7)	5.3(5)
C(12)	0.5674(8)	0.040(3)	0.4192(6)	3.7(4)
O(W1)	0.7322(9)	0.106(2)	0.0173(6)	7.7(4) *
O(W2)	0.389(2)	0.055(5)	0.952(1)	19(1) *

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

3. Results and discussion

3.1. Solid state

The ORTEP view of the complex molecule is reported with the atom numbering scheme in Fig. 1; bond distances and angles are given in Table 3.

The unit cell contains monomeric [Cu(ophen)(Cl-acgly)$_2$] units and lattice water molecules. The Cu(II) atom is strongly bonded to a carboxylic oxygen of each Cl-acgly molecule and to the nitrogens of the 1,10-phenanthroline molecule. The Cu–O and Cu–N bond distances are quite similar to those found in bis(N-acetylglycinato)-1,10-phen-anthrolinecopper(II) [12] and in other Cu-bpy ternary complexes with carboxylate ligands [5]. The short Cu–O bond distances [1.936(8) and 1.94(1) Å] could be due to the π back bonding from the metal to the aromatic amine. Two long contacts involve the uncoordinated carboxylic oxygens
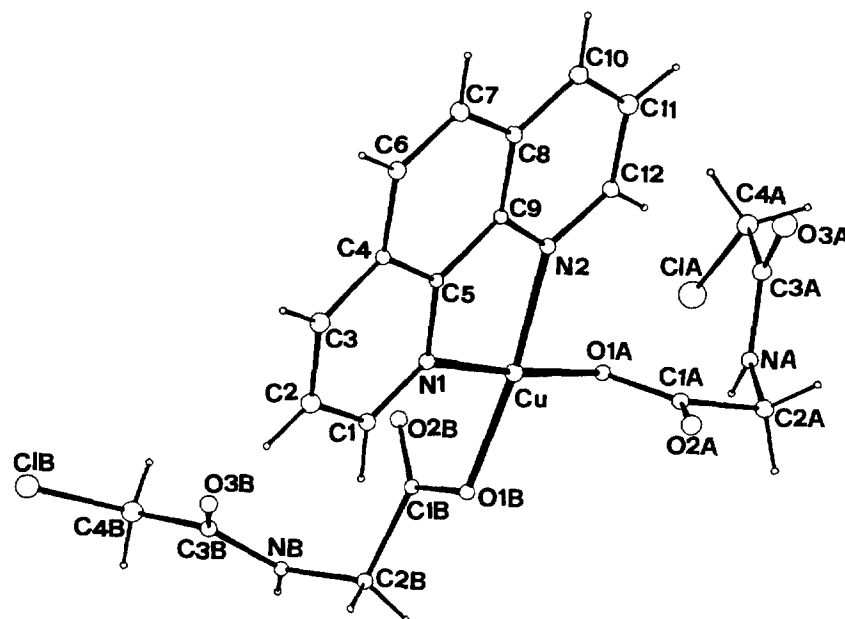
Fig. 1. ORTEP view of the [Cu(ophen)(Cl–acgly)₂] moiety with atom numbering scheme.

Cu⋯O(2A) 2.70(2) and Cu⋯O(2B) 2.75(1) Å with angles between the Cu⋯O vector and the normal to the coordination plane of 35.7 and 38.7°, respectively, suggesting an essentially square-planar arrangement for our complex.

The deviations of the donor atoms from the equatorial plane, within ±0.015 Å, are less than those observed in bis(N-acetylglycinato)-1,10-phenanthrolinecopper(II) [12] (±0.15 Å). Regarding the tetrahedral distortion in square-planar arrangement, the value of the dihedral angle between CuN₂ and CuO₂ planes is 1.5° in our complex while in the previously cited complex it was 12.2°.

The phenanthroline molecule is planar with an angle of 1.2° with the equatorial coordination plane; it forms a five-membered chelate ring with an angle at Cu (81.24°) in good agreement with the mean value (80.6°) found for copper(II)–phenanthroline complexes [12].

Bond distances and angles within the N-chloroacetylglycine molecules are normal and quite similar in the two independent ligand molecules. The only difference is observed in the carboxylic C–O bond lengths, which are different from one another in molecule B and quite similar in molecule A, as a consequence of the formation of a short contact with water molecule (O(2A)⋯O(W1)2.77(2) Å). The two independent ligand molecules differ also in the torsion angles: N–C(2)–C(1)–O(2) is 16(2)° and 159(1)° in molecules A and B respectively and Cl–C(4)–C(3)–N is 12(2)° in molecule A and 166(1)° in molecule B. The conformation of molecule A enables the Cl(A) atom to form a strong hydrogen bond involving N(A) [N(A)⋯Cl(A) 2.88(2) Å; H(3)⋯Cl(A) 2.35(4) Å; N(A)–H(3)⋯Cl(A) 112°] while Cl(1B) gives an interatomic contact with O(3B) [Cl(B)⋯O(3B)2.96(1) Å].

The lattice water molecules form short contacts with carboxylic and amidic oxygens (range 2.77–2.93 Å). Ring

stacking interactions between ophen rings involving the molecule at −x+1, y+1/2, −z+1/2 (range 3.57–3.80 Å) contribute to crystal packing (Fig. 2).

The electronic spectrum of the [Cu(ophen)(Cl–acgly)₂]·2H₂O complex shows a band envelope centered at 13 800–16 600 cm⁻¹ which indicates somewhat tetragonal distortion in the ligand field consistent with the weak apical interactions with oxygen atoms. This finding is in good agreement with the previously observed correlation between Cu⋯O axial distances, bipyramidal distortion angles and d–d band maximum position for square-planar complexes of N-protected amino acids [5].

In the corresponding bpy complex, the shift of the d–d band maximum at ≈ 15 600 cm⁻¹ may be more consistent with a square-pyramidal geometry, while the spectrum of the binary [Cu(Cl-acgly)₂]·2H₂O complex (d–d max. 16 100 cm⁻¹) is almost identical to that of [Cu(acgly)₂-(H₂O)₂]·2H₂O [13] suggesting the same square-planar coordination geometry for our complex.

The more relevant IR bands are assigned by comparison with the free ligand and the values are reported as supplementary material. No relevant differences are observed in the ν_NH of the solid complexes with respect to the free ligand, while the ν_CO is split in the structurally known complex, in accordance with the presence, in the unit cell, of two independent ligand molecules. This feature is maintained also in the bpy-containing ternary complex. The ν_C–Cl is shifted to lower energy in the [Cu(ophen)(Cl-acgly)₂]·2H₂O complex owing to the involvement of one chlorine atom in a strong hydrogen bond.

3.2. Solution study

The logarithm of the acid protonation constant and the overall stability constants of the complexes are reported in

Table 3
Bond distances (Å) and angles (°)

|			
Cu–O(1A)	1.936(8)	C(1B)–O(1B)	1.29(2)
Cu–O(1B)	1.94(1)	C(1B)–O(2B)	1.19(2)
Cu–N(1)	2.01(2)	N(1)–C(1)	1.32(2)
Cu–N(2)	2.01(1)	N(1)–C(5)	1.35(2)
Cl(A)–C(4A)	1.75(2)	C(1)–C(2)	1.39(2)
C(4A)–C(3A)	1.52(3)	C(2)–C(3)	1.36(2)
C(3A)–O(3A)	1.20(2)	C(3)–C(4)	1.39(3)
C(3A)–N(A)	1.31(2)	C(6)–C(7)	1.34(3)
N(A)–C(2A)	1.47(2)	C(6)–C(4)	1.41(2)
C(2A)–C(1A)	1.51(2)	C(7)–C(8)	1.44(2)
C(1A)–O(1A)	1.28(2)	C(10)–C(11)	1.35(2)
C(1A)–O(2A)	1.25(2)	C(10)–C(8)	1.40(3)
Cl(B)–C(4B)	1.74(2)	C(8)–C(9)	1.41(2)
C(4B)–C(3B)	1.51(3)	C(12)–N(2)	1.34(2)
C(3B)–O(3B)	1.23(1)	N(2)–C(9)	1.34(1)
C(3B)–N(B)	1.34(1)	C(4)–C(5)	1.41(1)
N(B)–C(2B)	1.45(2)	C(8)–C(9)	1.38(2)
C(2B)–C(1B)	1.56(3)	C(9)–C(5)	1.41(2)
O(1A)–Cu–O(1B)	94.5(4)	O(1B)–C(1B)–O(2B)	126(2)
N(1)–Cu–N(2)	81.0(7)	Cu–O(1B)–C(1B)	109(1)
O(1A)–Cu–N(1)	174.8(8)	C(1)–N(1)–C(5)	120(1)
O(1A)–Cu–N(2)	93.8(7)	N(1)–C(1)–C(2)	121(1)
O(1B)–Cu–N(1)	90.7(6)	C(1)–C(2)–C(3)	120(2)
O(1B)–Cu–N(2)	171.6(7)	C(2)–C(3)–C(4)	120(1)
Cl(A)–C(4)–C(3A)	116(2)	C(7)–C(6)–C(4)	121(1)
C(4)–C(3A)–O(3A)	119(2)	C(6)–C(7)–C(8)	122(1)
C(4)–C(3A)–N(A)	115(1)	C(11)–C(10)–C(8)	118(1)
O(3A)–C(3)–N(A)	126(2)	C(10)–C(11)–C(12)	122(2)
C(3A)–N(A)–C(2A)	119(1)	C(11)–C(12)–N(2)	121(1)
N(A)–C(2A)–C(1A)	114(1)	C(12)–N(2)–C(9)	118(1)
C(2A)–C(1A)–O(1A)	119(1)	C(3)–C(4)–C(6)	125(1)
C(2A)–C(1A)–O(2A)	118(2)	C(3)–C(4)–C(5)	116(1)
O(1A)–C(1A)–O(2A)	122(1)	C(6)–C(4)–C(5)	119(2)
Cu–O2A–C(1A)	109.1(9)	C(7)–C(8)–C(10)	124(1)
Cl(B)–C(4B)–C(3B)	112(1)	C(7)–C(8)–C(9)	118(2)
C(4B)–C(3B)–O(3B)	126(1)	C(10)–C(8)–C(9)	118(1)
C(4B)–C(3B)–N(B)	112(1)	N(2)–C(9)–C(8)	124(2)
O(3B)–C(3B)–N(B)	123(2)	N(2)–C(9)–C(5)	115(1)
C(3B)–N(B)–C(2B)	119(1)	C(8)–C(9)–C(5)	121(1)
N(B)–C(2B)–C(1B)	112(1)	N(1)–C(5)–C(4)	123(2)
C(2B)–C(1B)–O(1B)	111(1)	N(1)–C(5)–C(9)	118(1)
C(2B)–C(1B)–O(2B)	123(1)	C(4)–C(5)–C(9)	120(1)
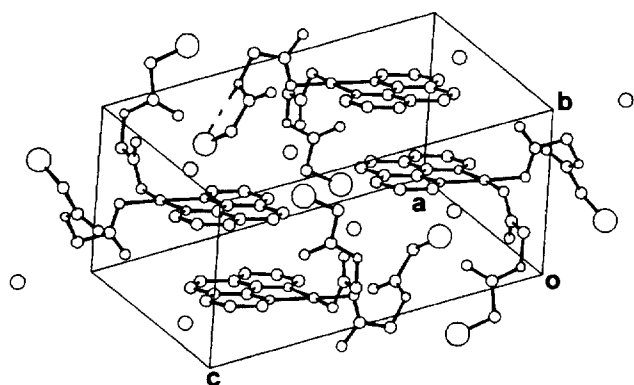
Fig. 2. Packing of the complex.

Table 4
Logarithm of protonation constant of N-chloroacetylglycine and log β of the complexes at 25°C and $I = 0.1$ mol dm^{-3} (NaNO$_3$) with e.s.d.s in parentheses

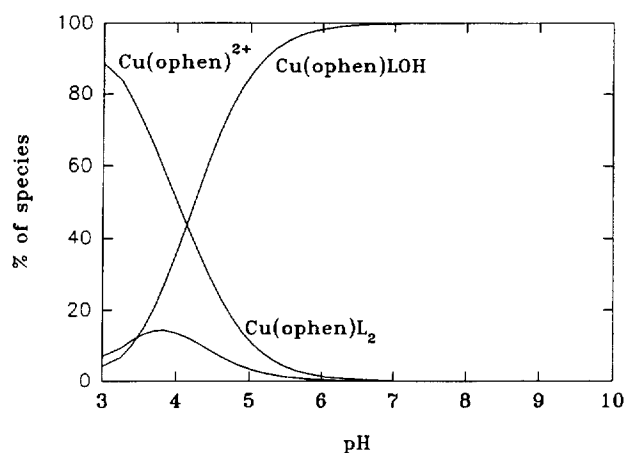| LH	log β_{0011}	3.264(3)	
[CuL$_2$]	log β_{1020}	4.11(4)	
		A = bpy	A = ophen
[CuAL$_2$]	log β_{1120}	12.43(7)	13.777(2)
[CuAL(OH)]	log β_{111-1}	5.92(3)	7.64(1)
[CuA]$^{2+}$	log β_{1100}	8.00 [a]	9.25 [a]
	log K [b]	4.43	4.52
	log K [c]	0.32	0.43

[a] Values taken from Ref. [14].
[b] log K = log β_{1120} − log β_{1100}.
[c] Δ log K = log K − log β_{1020}.

Fig. 3. Species distribution curves for the ternary system Cu^{2+}–bpy–Cl–acgly in the 1:1:4 molar ratio, [Cu^{2+}] = 2.5 × 10^{-3} mol dm^{-3}.

Table 4, while the species distribution curves for the bpy containing ternary system are given in Fig. 3. The titration of N-chloroacetylglycine in the 3–12 pH range revealed only one equivalent point corresponding to the dissociation of carboxyl. The pK_a value [3.264(3)] is smaller than that of N-acetylglycine (3.67) [15] and of the other N-acetyl or N-benzoyl amino acids [6,16] (range 3.35–3.80) indicating that the presence of a substituent with electrophilic effect, such as a chlorine atom, significantly affects the dissociation of the carboxyl group. The potentiometric titration for all metal-to-ligand molar ratios investigated exactly corresponds to that of the ligand up to pH ≈ 6, suggesting that the only active binding site is the carboxyl, which is known to possess a very weak coordination ability. In processing the data the species [CuL]$^+$ and [CuL$_2$] were taken into account but the better convergence was obtained with [CuL$_2$]. Its calculated log β value of 4.11(4) is similar to that found in other Cu(II)-N-acetyl- and Cu(II)-N-benzoyl amino acid systems while it is rather lower than that observed in Cu(II)-ArSO$_2$-N-protected amino-acid systems (mean value 5.2) [17,18]. As a result it could be separated as the solid microcrystalline binary compound of empirical formula Cu(Cl-acgly)$_2$ · 2H$_2$O only from a very concentrated solution.

The pH-metric titration curves of the ternary systems show two equivalence points, the first corresponding to the complete dissociation of the carboxylic group, while the second, which is accompanied by a color change from pale blue to deep blue, is attributed to the formation of a mixed hydroxo species [CuALOH]. The precipitation of copper hydroxide does not occur, even beyond pH 11. Spectrophotometric analysis at the metal-to-ligand molar ratio of 1:4 shows a titration pattern with a shift of the d–d band maximum from 680 nm at pH 6.1 to 620 and 645 nm at pH 11.5 for the bpy- and ophen-containing systems, respectively. The same behavior was previously found in the corresponding Cu(II) ternary systems with 4-NO_2-hippuric acid; accordingly, the processing of data takes the same species [$CuAL_2$] and [CuALOH] into account.

The calculated $\Delta \log K$ values of 0.32 and 0.43 for bpy and ophen, respectively, confirm the selective effect of these amines toward carboxylate ligands. These values are smaller than those observed for the same ternary complexes with hydantoic acid (-0.26, -0.05) which suggests that, by enhancing the capability of our ligand to interact with the solvent to form hydrogen bonds, the presence of a chlorine atom plays an important role in stabilizing the ternary complexes. In the case of the corresponding 4-NO_2-hippuric acid systems [6], the greater stability of the ternary complexes, as shown by the $\Delta \log K$ values of 0.84 and 0.86, could be attributed to the possible retention in the aqueous solution of ring-stacking interactions involving the amino acid molecule. The possible involvement of the chlorine atom in intra- or intermolecular hydrogen bonds, which are found in the solid state, could be responsible of the fact that one L ligand is more readily substituted for one hydroxide ion than in the case of 4-NO_2-hippuric acid, thus leading to a more stable mixed hydroxo complex already formed at pH ≈ 5.

4. Supplementary material

Thermal parameters, atomic parameters for hydrogen atoms, a list of observed and calculated structure factors and more relevant IR bands are available from the authors upon request (21 pages).

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