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Mono-Amino-Acid–Copper Complexes: Syntheses and Structures of Chloro(glycinato)(methanol)copper(II) and Chloro(glycinato)(1-methylimidazole)copper(II)

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Abstract. Chloro(glycinato)(methanol)copper(II) (1), $[CuCl(C_2H_4NO_2)(CH_4O)]$, $M_r = 205{\cdot}04$, monoclinic, $P2_1/c$, $a = 5{\cdot}192$ (3), $b = 7{\cdot}945$ (5), $c = 16{\cdot}51$ (1) Å, $\beta = 100{\cdot}24$ (5)°, $V = 670{\cdot}2$ (7) Å^3, $Z = 4$, $D_x = 2{\cdot}03$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 78{\cdot}6$ cm^{-1}, $F(000) = 412$, $T = 293$ K, $R = 0{\cdot}041$, 789 unique observed reflections. Chloro(glycinato)(1-methylimidazole)copper(II) (2), $[CuCl(C_2H_4NO_2)(C_4H_6N_2)]$, $M_r = 255{\cdot}09$, orthorhombic, $Pca2_1$, $a = 24{\cdot}97$ (2), $b = 4{\cdot}009$ (1), $c = 9{\cdot}116$ (7) Å, $V = 913$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}84$, $D_x = 1{\cdot}86$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 59{\cdot}1$ cm^{-1}, $F(000) = 516$, $T = 293$ K, $R = 0{\cdot}062$, 575 unique observed reflections. The Cu atom in (1) has four close, equatorial ligating atoms (NO_2Cl) and two, more distant, axial ligating atoms (ClO). Molecules of (2) are linked through μ_2-Cl atoms forming polymeric zigzag chains in the solid state with adjacent chains joined by hydrogen bonds involving the glycinate. The Cu atom has four close ligating atoms (N_2OCl) and an axial chlorine ligand at 2·883 Å.

Introduction. There has been considerable interest in structural studies of Cu^{II} complexes of amino acids and small polypeptides, both as actual species present in biological systems (Freeman, Guss, Healy, Martin & Nockolds, 1969; Ono, Shimanouchi, Sasada, Sakurai, Yamauchi & Nakahara, 1979; Pickart, Freedman, Loker, Peisach, Perkins, Stenkamp & Weinstein, 1980; Perkins, Stenkamp, Weinstein, Pickart, Rose & Jensen, 1984) and as potential model compounds for copper-containing metalloproteins (Freeman, 1967). Much of this interest has been directed towards the study of bis amino-acid complexes. To date, four crystal structures of mixed amino-acid complexes (Freeman *et al.*, 1969; D'yakon, Kairyak, Chapurina & Ablov, 1978; Ono *et al.*, 1979; Ono & Sasada, 1981) and ten crystal structures which contain ligands in addition to amino acids or water (Neitzel & Desiderato, 1975; Stephens, Vagg & Williams, 1977; Antolini, Marcotrigiano, Menabue, Pellacani & Saladini, 1982; Colyvas, Tietze & Egri, 1982; Antolini, Marcotrigiano, Menabue & Pellacani, 1983; Antolini, Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1986; Duarte, Carrondo, Simões Gonçalves, Hursthouse, Walker & Dawes, 1986; Aoki & Yamazaki, 1987; Solans, Ruiz-Ramírez, Martinez, Gasque & Briansó, 1988) have been reported. We report here the syntheses and structures of two additional ternary amino-acid complexes of Cu^{II}, chloro(glycinato)(methanol)copper(II) (1) and chloro(glycinato)(1-methylimidazole)copper(II) (2).

Experimental. *Syntheses.* Compound (1). Copper(II) chloride dihydrate (2·0459 g, 12 mmol) was dissolved in 100 ml of methanol, and glycine (1·8024 g, 24 mmol) was added. From this heterogeneous mixture (glycine is only slightly soluble in methanol), (1) is formed as a blue powder in minutes (yield 2·0582 g, 84% based on copper).

X-ray-quality crystals were obtained by the following procedure. Copper(II) chloride dihydrate (0·3415 g, 2 mmol) was dissolved in 30 mL of methanol. A slurry of glycine (0·1502 g, 2 mmol) and sodium methoxide (0·1093 g, 2 mmol), which had been stirred in 60 mL of methanol for 30 min, was added to the copper(II) chloride solution in three portions over a period of 15 min with just enough stirring to dissolve the solids after each addition. After 2d, clusters of irregular blue crystals of compound (1) were obtained (yield 0·2777 g, 68% based on copper). If the solution is stirred too vigorously, a blue powder of (1) results. Before elemental analysis, the sample was dried *in vacuo* over P_4O_{10}. Analysis: calculated for $C_3H_8NO_3ClCu$: C 17·57, H 3·93, N 6·83, Cl 17·29, Cu 30·98; found: C 17·63, H 3·94, N 6·85, Cl 16·73, Cu 30·73%.

Compound (2). To compound (1) (1·0334 g, 5·0 mmol) dissolved in 100 mL of methanol was added 5·0 mL of a 1·00 *M* solution of 1-methyl-

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Table 1. *Crystal data and data collection details*

	Compound (1)	Compound (2)
Crystal size (mm)	0·10 × 0·16 × 0·40	0·67 × 0·40 × 0·03
Diffractometer type	Picker Automatic FACS-1	
No. reflections used for cell-constant determination	20 at $2\theta = 58$ to 74°	8 equivalent reflections at $2\theta = 51·9°$
Scan type	$\omega/2\theta$	
2θ range (°)	2–110	
Scan rate[a] (° min^{-1})	2 in 2θ	4 in 2θ
Standard reflections	5 every 90 min	3 every 60 min
Deterioration correction max.	None made	1·163
No. unique data collected (excluding absences)	845	625
Criterion for observeds	$F_o \geq 4\sigma(F_o)$	
Range of absorption factors[b]	1·0–1·641	1·0–2·885
Coincidence loss[c] ($\times 10^{-8}$)	8·624529	55·01901
Reflections measured	$-h, -k, \pm l$	$+h, +k, +l$
Final R	0·041	0·062
Final wR	0·049	0·061
Goodness of fit	6·4049	2·3597
No. contributing reflections	823	599
$(\Delta/\sigma)_{max}$	0·684	0·383
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2·5, −1·6	1·6, −1·1

Notes: (*a*) Backgrounds were collected for 10 s on either side of the reflection using a stationary counter–stationary crystal technique. (*b*) Method used was that of North, Phillips & Mathews (1968). (*c*) Method used was that of Sletten, Sletten & Jensen (1969). (*d*) $w = 1/\sigma_F^2$. Scattering factors for Cu, Cl, C, O and N taken from Cromer & Mann (1968), scattering factor for H taken from Stewart, Davidson & Simpson (1965), anomalous-dispersion terms for Cu and Cl (both f' and f'') taken from *International Tables for X-ray Crystallography* (1962).

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters of the non-*H *atoms of chloro(glycinato)(methanol)copper*(II)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}(Å^2)
Cu	0·98037 (17)	0·42577 (11)	0·38209 (5)	0·0384
Cl	1·20227 (33)	0·30117 (20)	0·49565 (9)	0·0492
N	1·2377 (11)	0·6049 (6)	0·3827 (3)	0·046
C(1)	1·1413 (13)	0·7341 (8)	0·3253 (4)	0·048
C(2)	0·8710 (12)	0·6928 (8)	0·2779 (3)	0·037
C(3)	0·6972 (16)	0·0897 (9)	0·3962 (5)	0·065
O(1)	0·7620 (7)	0·5624 (5)	0·2974 (2)	0·035
O(2)	0·7736 (8)	0·7931 (5)	0·2217 (3)	0·049
O(3)	0·6996 (8)	0·2581 (5)	0·3660 (3)	0·050

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters of the non-*H *atoms of chloro(glycinato)(1-methylimidazole)copper*(II)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}(Å^2)
Cu	0·10304 (9)	−0·06343 (63)	0·50000	0·047
Cl	0·1533 (2)	0·3419 (12)	0·3873 (6)	0·050
N(1)	0·1458 (6)	−0·0857 (41)	0·6782 (18)	0·048
N(2)	0·1737 (6)	−0·2258 (44)	0·9035 (17)	0·051
N(3)	0·0546 (6)	−0·0818 (39)	0·3331 (17)	0·054
O(1)	0·0457 (4)	−0·3054 (38)	0·6016 (13)	0·055
O(2)	−0·0421 (5)	−0·4329 (35)	0·5852 (15)	0·058
C(1)	0·1348 (7)	−0·2390 (52)	0·8063 (22)	0·046
C(2)	0·1975 (8)	0·0409 (62)	0·7028 (26)	0·052
C(3)	0·2145 (7)	−0·0438 (55)	0·8352 (23)	0·051
C(4)	0·1731 (8)	−0·3478 (66)	1·0479 (22)	0·056
C(5)	−0·0003 (7)	−0·1695 (51)	0·3883 (22)	0·068
C(6)	−0·0009 (7)	−0·3048 (48)	0·5287 (19)	0·062

imidazole ($C_4H_6N_2$) in methanol (3·98 mL of 1-methylimidazole diluted to 50 mL with methanol). The volume of the resulting solution was reduced by half through rotary evaporation. After 2–4d, both blue and yellow crystals appeared. The blue sail-shaped plates are compound (2) (yield 0·2921 g, 23% based on copper), while the yellow crystals are [Cu_4OCl_6(l-Meim)$_4$] (Norman, 1985), a minor by-product (yield 0·0182 g, 0·4% based on copper). Density measured by flotation method using C_2H_2Br and CCl_4. Before elemental analyses, the blue crystals were drived *in vacuo* over P_4O_{10}. Analysis: calculated for $C_6H_{10}N_3O_2ClCu$: C 28·24, H 3·95, N 16·47, Cl 13·89, Cu 24·90; found: C 28·11, H 3·91, N 16·37, Cl 13·85, Cu 24·60%.

Crystal and X-ray data. Crystals of compound (1) after drying gave powder diffraction patterns. To obtain single-crystal diffraction data, an irregular, roughly prismatic, blue, crystal of (1) was mounted in a glass capillary sealed with mother liquor, silicone oil, and silicone-based stopcock grease. Crystals of compound (2) also give powder patterns unless mounted in capillaries with the mother liquor. Pertinent details regarding crystal data, intensity-data collection, and full-matrix least-squares refinement of the two structures are collected in Table 1. The pattern of systematic extinctions found in compound (1) ($0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$) determine the space group to be $P2_1/c$. The pattern of systematic extinctions found in compound (2) ($h0l$, $h = 2n + 1$ and $0kl$, $l = 2n + 1$) is consistent with the space group $Pca2_1$ or an alternate setting of the space group $Pbcm$. The lower-symmetry space group ($Pca2_1$) was chosen, and the subsequent solution and refinement of the structure confirmed the choice. Both structures were solved using conventional heavy-atom methods. For compound (1), the methanol H atoms were located in difference maps and not refined. For compound (2), seven of the ten H atoms were found in difference maps, while three were placed in their calculated positions. All were refined through one cycle of least squares and then fixed. For both compounds the function minimized by the method of least squares was $\sum w(|F_o| - |F_c|)^2$ using $1/\sigma^2$ weights where $\sigma(F)$ was derived using $\sigma^2(F^2) =$ [gross counts + ($k \times$ net counts)^2], where $k = 0·01$ for (1) and 0·03 for (2), and $\sigma(F) = [F^2 + \sigma(F^2)]^{1/2} - (F^2)^{1/2}$. The *XRAY*76 programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) were used throughout the computations. The data set for (1) was corrected for coincidence loss, while both (1) and (2) were corrected for Lorentz, polarization, and absorption effects. An empirical deterioration correction was applied to the data for compound (2).

Tables 2 and 3 list the fractional atomic coordinates for compounds (1) and (2) respectively.*

Discussion. Figs. 1 and 2 show the molecular structures of compounds (1) and (2), and Figs. 3 and 4 show stereoviews of each unit cell respectively. The Cu atom in (1) has a coordination polyhedron with four relatively short equatorial interactions (with N of glycine, one O of glycine, Cl, and O of methanol) and two longer, axial interactions involving a Cl atom and the other O atom of glycine, see Fig. 5. The bond distances and angles are listed in Table 4. The Cu, Cl, O (of methanol), and N atoms very nearly describe a plane, with the O atom of glycine displaced perpendicularly from this plane by 0·39 Å away from the axial O atom. The standard deviation of the defining atoms from this plane is 0·010 Å. The r.m.s. displacement of the defining atoms from the least-squares best-fit plane through the four equatorial ligating atoms is 0·130 Å, and the Cu atom is displaced from this plane by 0·08 Å towards the axial O atom.

The coordination polyhedron of the Cu atom in compound (2) can be described as a square pyramid [basal plane defined by Cl,O,N (of glycine) and N (of 1-Meim); Cl at the apex] distorted towards a trigonal bipyramid (two Cl atoms and the O atom in the equatorial plane), see Fig. 6. The bond distances are also listed in Table 4.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52179 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

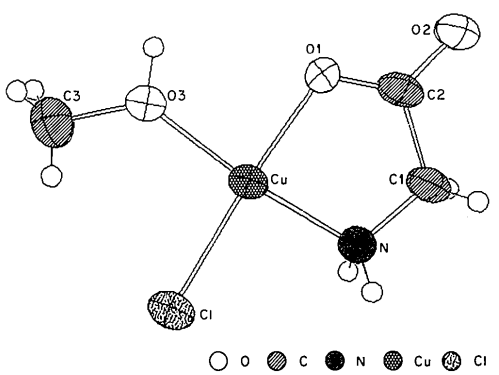

Fig. 1. Molecular structure of chloro(glycinato)(methanol)copper-(II) illustrating the atomic numbering scheme.

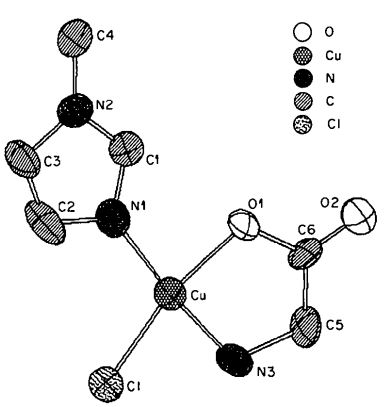

Fig. 2. Molecular structure of chloro(glycinato)(1-methylimidazole)copper(II) illustrating the atomic numbering scheme.

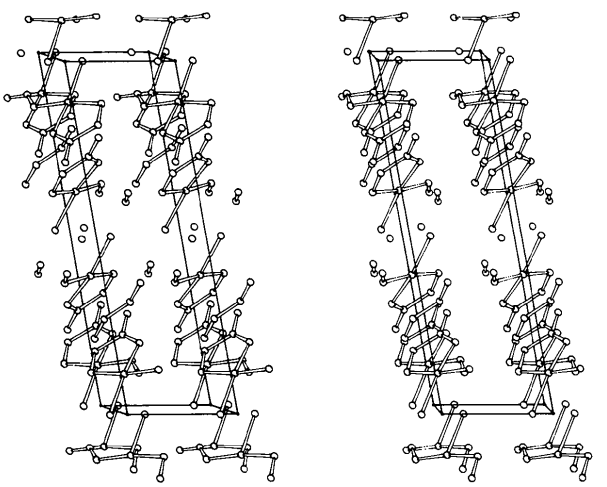

Fig. 3. Stereoscopic view down **b** of the unit cell for chloro-(glycinato)(methanol)copper(II).

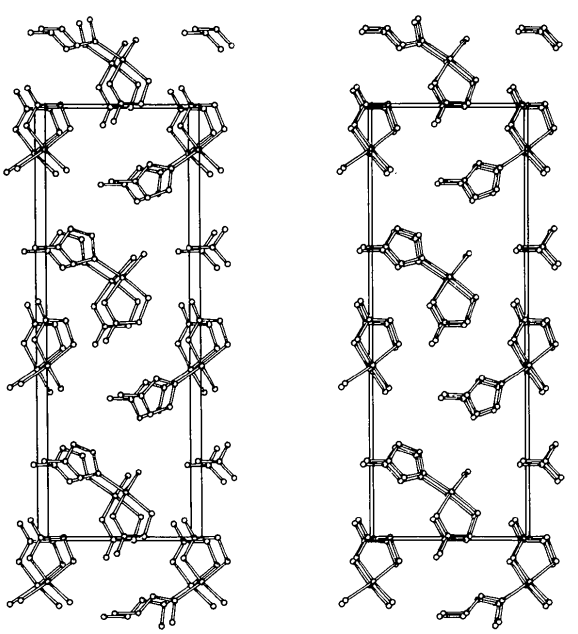

Fig. 4. Stereoscopic view down **b** of the unit cell for chloro-(glycinato)(1-methylimidazole)copper(II).

In both complexes, the copper—ligand distances are within the normal ranges of such distances, with the exception of the Cu—O(methanol) distances in (1), 1·958 (4) Å. This distance is significantly shorter than the reported ranges for both non-cubane-like copper compounds in which the methanol occupies an axial position [2·159 (7) to 2·477 (2) Å], and cubane-like copper compounds in which the methanol coordination is intermediate between axial and equatorial (or basal) (2·04 to 2·08 Å) (Ablov, Simonov, Matuzenko, Dvorkin, Yampol'skaya & Malinovskii, 1977). We are not aware of any previously reported Cu–methanol complexes containing methanol in an equatorial position as found in compound (1). The distances within the methanol, 1-methylimidazole, and glycinate moieties are all within the expected ranges.

The axial interactions in both compounds are significant. In his discussion of coordination numbers and bond orders in metal–peptide complexes, Freeman (1967) assigns a bond order of 0·75 to Cu—O distances in the range of 2·5 to 2·6 Å [the distance in (1) is 2·542 (4) Å]. It should be emphasized that the Cu atom in compound (1) is not significantly displaced towards either the axial Cl atom or the axial O atom, indicating that the Cu–Cl axial interaction is as significant as the Cu–O axial interaction.

In the crystalline state, see Figs. 5 and 6, both of these compounds pack such that the Cl atom, in addition to being tightly bound to the copper, also serves as an axial ligand for a symmetry-related Cu

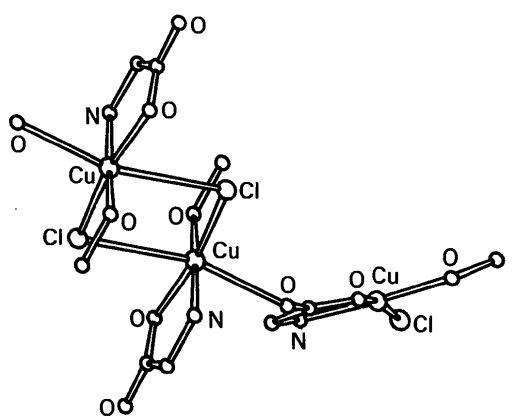

Fig. 5. Drawing showing chloro(glycinato)(methanol)copper(II) molecules binding to adjacent molecules through μ_2-bridging O and Cl atoms.

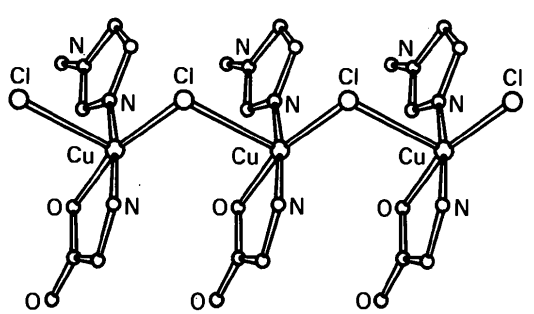

Fig. 6. Drawing showing adjacent chloro(glycinato)(1-methylimidazole)copper(II) molecules linking through μ_2-bridging Cl atoms.

Table 4. *Selected bond distances, non-bonding distances* (Å), *and angles* (°) *for chloro(glycinato)-(methanol)copper*(II) *and chloro(glycinato)-(1-methylimidazole)copper*(II)

Chloro(glycinato)(methanol)copper(II)

Cu—Cl	2·249 (2)	Cu—O(2^{ii})	2·540 (5)
Cu—N	1·951 (5)	C(1)—C(2)	1·517 (8)
Cu—O(1)	1·964 (4)	C(1)—N	1·426 (8)
Cu—O(3)	1·958 (4)	C(2)—O(1)	1·250 (7)
Cu—Cl^{i}	3·218 (2)	C(2)—O(2)	1·259 (7)

Cl—Cu—N	93·9 (1)	N—Cu—O(2^{ii})	83·1 (2)
Cl—Cu—O(1)	169·4 (1)	O(1)—Cu—O(3)	87·5 (2)
Cl—Cu—O(3)	94·2 (1)	O(1)—Cu—Cl^{i}	83·0 (1)
Cl—Cu—Cl^{i}	86·5 (1)	O(1)—Cu—O(2^{ii})	92·6 (1)
Cl—Cu—O(2^{ii})	97·8 (1)	O(3)—Cu—Cl^{i}	104·4 (1)
N—Cu—O(1)	84·8 (2)	O(3)—Cu—O(2^{ii})	94·4 (2)
N—Cu—O(3)	171·8 (2)	Cl^{i}—Cu—O(2^{ii})	160·4 (1)
N—Cu—Cl^{i}	77·5 (2)		

Cu—Cl—Cu^{i}	93·6 (1)	Cu—N—C(1)	111·2 (4)
C(2)—C(1)—N	111·8 (5)	Cu—O(1)—C(2)	114·3 (3)
C(1)—C(2)—O(1)	117·8 (5)	C(2)—O(2)—Cu^{iii}	125·1 (4)
C(1)—C(2)—O(2)	117·2 (5)	Cu—O(3)—C(3)	129·9 (4)
O(1)—C(2)—O(2)	125·0 (5)		

Superscripts denote atoms related to those at x, y, z as follows: (i) $2·0-x$, $1·0-y$, $1·0-z$; (ii) $2·0-x$, $y-0·5$, $0·5-z$; (iii) $2·0-x$, $0·5+y$, $0·5-z$.

Chloro(glycinato)(methylimidazole)copper(II)

Cu—Cl	2·296 (5)	C(1)—N(1)	1·35 (3)
Cu—Cl^{i}	2·883 (5)	C(1)—N(2)	1·32 (2)
Cu—N(1)	1·946 (16)	C(2)—N(1)	1·40 (3)
Cu—N(3)	1·946 (15)	C(3)—C(2)	1·32 (3)
Cu—O(1)	1·963 (13)	C(3)—N(2)	1·40 (3)
		C(4)—N(2)	1·40 (3)
		C(5)—C(6)	1·39 (3)
		C(5)—N(3)	1·50 (2)
		C(6)—O(1)	1·34 (2)
		C(6)—O(2)	1·26 (2)

Cl—Cu—Cl^{i}	100·8 (2)	N(1)—C(1)—N(2)	114 (2)
Cl—Cu—N(1)	96·1 (5)	C(3)—C(2)—N(1)	110 (2)
Cl—Cu—N(3)	91·0 (5)	C(2)—C(3)—N(2)	108 (2)
Cl—Cu—O(1)	163·8 (4)	C(6)—C(5)—N(3)	114 (1)
Cl^{i}—Cu—N(1)	91·2 (5)	C(5)—C(6)—O(1)	117 (2)
Cl^{i}—Cu—N(3)	87·8 (5)	C(5)—C(6)—O(2)	123 (2)
Cl^{i}—Cu—O(1)	94·4 (4)	O(1)—C(6)—O(2)	120 (2)
N(1)—Cu—N(3)	172·9 (7)	C(1)—N(1)—C(2)	102 (2)
N(1)—Cu—O(1)	89·1 (6)	Cu—N(1)—C(1)	129 (1)
N(3)—Cu—O(1)	84·0 (6)	Cu—N(1)—C(2)	128 (1)
		C(1)—N(2)—C(3)	105 (2)
		C(1)—N(2)—C(4)	128 (2)
		C(3)—N(2)—C(4)	127 (2)
		Cu—N(3)—C(5)	108 (1)
		Cu—O(1)—C(6)	114 (1)

Superscript (i) denotes atoms related to those at x, y, z by the operation x, $y-1·0$, z.

atom. However, the compounds do not show identical bridging patterns. (2) exhibits a zigzag pattern of bridging Cl atoms, while (1) has a more complex pattern of bridging involving both Cl atoms and the carboxylate O atom of glycine. In (1), there is also a strong hydrogen bond involving methanol and the carboxylate O atom of glycine, O—O distance 2·636 (6) Å. We believe it possible that this hydrogen-bonding interaction, combined with the difference in the close coordination configurations [N_2OCl for (2) and NO_2Cl for (1)], leads to the difference in bridging patterns.

The crystals of (1) and (2) change upon their removal from the mother liquor. The crystals become amorphous in appearance and give rise to X-ray diffraction powder patterns. However, compound (1) is stable for several weeks in a sealed capillary in the presence of the mother liquor. Also, when it is dried for about 10 h at room temperature *in vacuo* over P_4O_{10}, the weight loss is less than 0·1%. The change that compound (1) undergoes in air can be inferred from elemental analyses of samples that were exposed to air. These analyses are consistent with the methanol in the crystals being replaced by water:

$$[CuCl(gly)(MeOH)]_{(s)} + xH_2O_{(g)} \longrightarrow CuCl(gly)(H_2O)_{x(g)} + MeOH_{(g)}.$$

Attempts to recrystallize compound (1) from water have not been successful. The infrared spectrum of one of the products of recrystallization is that of *cis*-$Cu(gly)_2.H_2O$ (Condrate & Nakamoto, 1965):

$$[CuCl(gly)(MeOH)]_{(s)} \xrightarrow[H_2O]{} \textit{cis}\text{-}Cu(gly)_2.H_2O_{(s)} + \text{other products.}$$

It seems reasonable to conclude that compound (1) is a unique product associated with preparation in methanol.

The pattern of change observed for compound (2) is more complicated. If the crystals are left in contact with the mother liquor for a period of weeks, they are replaced by a mixture of yellow crystals of the same crystal habit as $[Cu_4OCl_6(1\text{-Meim})_4]$ which has always been found as a by-product in the preparation of compound (2), and small, fine blue crystals which have the same crystal habit as *cis*-$Cu(gly)_2.H_2O$. It was observed that several weeks after the X-ray data for compound (2) were collected, the single crystal was gone, and a myriad of extremely small yellow crystals and blue crystals filled the space previously occupied by the single crystal. From this we infer that compound (2) is a kinetic product of this system, while $[Cu_4OCl_6(1\text{-Meim})_4]$ is one of the thermodynamic products. This implies that while (2) appears to be the obvious product of a simple replacement of methanol by 1-methylimidazole, the situation is more complicated as summarized by the following reactions:

$$[CuCl(gly)(MeOH)]_{(s)} + 1\text{-Meim} \xrightarrow[MeOH]{} [CuCl(gly)(1\text{-Meim})]_{(s)} \text{ (preparation)}$$

$$yH_2O + x[CuCl(gly)(1\text{-Meim})]_{(s)} \longrightarrow [Cu_4OCl_6(1\text{-Meim})_4]_{(s)} + Cu(gly)_2.H_2O + \text{other products (on standing).}$$

If (2) is a kinetic product, then the formation of crystalline (2) must be driven in part by the relative insolubility of (2) in this solvent system compared to the various other species in the reaction mixture.

The transformations mentioned above severely complicate attempts to obtain other physical measurements of compounds (1) and (2).

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Structure of a Copper(II) Complex of 2-*C*-Carboxypentonic Acid (H_3cpa); $[Cu_9Br_2(cpa)_6]_n^{2-}.xH_2O$

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Abstract. $[Cu_9Br_2(C_6H_7O_6)_6]_n^{2-}.xH_2O$, where $C_6H_7O_6^{3-}$ is 2-*C*-carboxypentonate (cpa^{3-}), trigonal, *P*321, $a = b = 21{\cdot}273\ (10)$, $c = 8{\cdot}0168\ (11)$ Å, $V = 3141{\cdot}9\ (2{\cdot}1)$ Å^3, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 28{\cdot}9$ cm^{-1}, $F(000) = 877$ (ignoring water molecules), $T = 293$ K, $R = 0{\cdot}081$ for 1182 unique observed reflections. The structure contains copper in two distinct environments, one of which is five-coordinate and the other six-coordinate. cpa^{3-} is a heptadentate ligand to three Cu atoms. Channels of disordered solvent occupy a major fraction of the cell volume.

Introduction. We have recently reported the structure and synthesis of $[Cu_9Cl_2(cpa)_6]_n^{2-}.xH_2O$, where cpa^{3-} is 2-*C*-carboxypentonate, from Cu^{II} and dehydroascorbic acid (Norman, Rose & Stenkamp, 1987). That structure appeared to contain a large amount of disordered solvent, and to determine whether those observations were real or were due to some computational or experimental problem, we also carried out the synthesis and structure of the bromine derivative, $[Cu_9Br_2(cpa)_6]_n^{2-}.xH_2O$, (2).

Experimental. $CuCl_2.2H_2O$ (0·8528 g, 5·0 mmol) was dissolved in 50 ml H_2O. Glycine (0·3760 g, 5·0 mmol) was then added, followed by the addition of ascorbic acid (0·4400 g, 2·5 mmol). The resulting suspension of CuCl was stirred for 30 min and filtered. KBr (2·9749 g, 25 mmol) was added to the filtrate, followed by the addition of copper(II) acetate hydrate (0·498 g, 2·5 mmol). After three days, blue trapezoidal prismatic crystals of (2) were formed.

A crystal (0·10 × 0·27 × 0·30 mm) was mounted in a glass capillary and sealed with mother liquor and silicone oil. Oscillation and Weissenberg photographs indicated that the cell was isomorphous with that of the chlorine derivative. On a Picker FACS-1, cell constants and e.s.d.'s at 293 K were determined from the least-squares refinement of 18 reflections with $60 < 2\theta < 71°$. Data were collected from 2 to 110° in 2θ using $\omega/2\theta$ scans with a scan speed of 2° min^{-1} in 2θ. Of the 1453 reflections measured, 1182 had F_o greater than $4\sigma(F_o)$. h 0–19, k 0–19, l 0–8. Backgrounds were collected for 10 s on either side of the reflection using a stationary-counter–stationary-crystal technique. Five standard reflections were collected every 90 min. The data were corrected for absorption using the empirical method of North, Phillips & Mathews (1968) (minimum value 1·000, maximum value 1·243), deterioration (maximum value of 1·024), and coincidence loss [Sletten, Sletten & Jensen (1969), $\tau = 7{\cdot}273467 \times 10^{-8}$]. The structure was solved by using the Cu-atom positions of the chlorine compound and conventional heavy-atom techniques. Atomic scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion terms for Cu and Br (f' and f'') were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a VAX 11/780 using the *XRAY* system (Stewart *et al.*, 1976).

Full-matrix least-squares refinement was not well behaved as evidenced by the need to treat many of the atoms with isotropic temperature factors. The maximum shift/e.s.d. on the last cycle was 0·32, but the current model includes a $(\sin\theta)/\lambda$ cutoff of 0·100 Å^{-1} (which excludes 14 low-resolution reflections more seriously affected by the disordered solvent), anisotropic thermal parameters for the Cu and

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