N(1)*RS*, N(2)*SR*, N(3)*RS*, N(4)*RS*, N(5) formally achiral (1*RS*, 7*SR*, 11*RS*, 14*RS* in systematic nomenclature). The six-membered chelate ring including N(1) and N(2) has a regular chair conformation while that including N(3) and N(4) has a symmetric skew-boat conformation. The five-membered chelate ring in the equatorial plane containing N(2) and N(3) has a half-chair conformation, while the two axial rings containing N(1), N(5) and N(4), N(5) are best described by an envelope conformation. Some strain within the macrocycle is evidenced by moderate deviations from ideal angles at N and C atoms. For example, in the six-membered rings, the mean of the bond angles at C is 113·6 (5)°, close to the value (113·5°) in the isomeric 17-membered macrocyclic complexes chloro(1,4,7,10,14-pentaazacycloheptadecane)cobalt(III).

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Structure of *catena*-Poly{[μ-(*N*-acetyl-DL-valinato)-O^1:O^3]-copper(II)}

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Abstract. $[Cu(C_7H_{12}NO_3)_2]_n$, $M_r = 379{\cdot}9$, triclinic, $P\bar{1}$, $a = 5{\cdot}687\,(4)$, $b = 6{\cdot}224\,(1)$, $c = 12{\cdot}634\,(2)$ Å, $\alpha = 95{\cdot}48\,(1)$, $\beta = 89{\cdot}80\,(4)$, $\gamma = 98{\cdot}46\,(4)°$, $V = 440{\cdot}3\,(3)$ Å^3, $Z = 1$, $D_m = 1{\cdot}44$ (by flotation), $D_x = 1{\cdot}43$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 12{\cdot}7$ cm^{-1}, $F(000) = 199$, $T = 293$ K, $R = 0{\cdot}053$ from 1514 observed reflections. The Cu atom lies on the symmetry center and displays a square-planar geometry arising from coordination of one carboxylic O and one peptidic O belonging to different ligand molecules, giving rise to a polymeric structure.

Introduction. We have previously observed that on increasing the hydrophobic character of *N*-acetyl amino acids the hydration of the blue binary complex decreases almost regularly. In blue [Cu(*N*-acetylglycinato)$_2$(H$_2$O)$_2$].2H$_2$O (Marcotrigiano, Pellacani, Battaglia & Bonamartini Corradi, 1976) and [Cu(*N*-acetyl-β-alaninato)$_2$(H$_2$O)$_2$] (Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1981) the same essentially square-planar coordination geometry with the CuO$_4$ chromophore is found and the metal environment derives from the carboxylate O atoms of the amino acid molecules, acting as monodentate ligands, and water O atoms. The uncoordinated carboxyl O gives rise to a weak interaction in the out-of-plane axial position, while the peptide group is only involved in hydrogen bonds. *N*-Acetyl-DL-valine forms a blue anhydrous complex for which the electronic spectrum (Marcotrigiano, Menabue & Pellacani, 1980) similarly suggested a square-planar geometry although this is not explained by the usual binding mode of *N*-acetyl amino acids.

Now, in order to verify the probable presence of a new binding mode of this class of ligand, we report here the crystal and molecular structure of *catena*-poly{[μ-(*N*-acetyl-DL-valinato)-O^1:O^3]-copper(II)}.

Experimental.

Preparation of the complex. The complex was prepared by adding a copper(II) perchlorate hexahydrate (1 mmol) solution in anhydrous ethanol to an *N*-acetyl-DL-valine (2 mmol) solution, neutralized with a stoichiometric amount of potassium hydroxide, in anhydrous ethanol. The potassium perchlorate precipitated was filtered off and, on standing for several

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days, microcrystals precipitated. By subsequent recrystallizations in 50% (*v*/*v*) methanolic/ethanolic solution, crystals suitable for X-ray analysis were obtained (found: C, 44·10; H, 6·40; N, 7·20%; calculated for $C_{14}H_{24}CuN_2O_6$: C, 44·24; H, 6·37; N, 7·38%).

Blue crystals (0·20 × 0·22 × 0·35 mm) were mounted on an Enraf–Nonius CAD-4 single-crystal X-ray diffractometer, Mo $K\alpha$ radiation (graphite monochromator), lattice parameters from setting of 25 reflections with $8 \leq \theta \leq 15°$; 1518 unique reflections with $\theta \leq 25°$; $-6 \leq h \leq 6$, $-7 \leq k \leq 7$, $0 \leq l \leq 15$; ω–2θ scan, scan width $(1{\cdot}2 + 0{\cdot}35\tan\theta)°$, scan speed 1·27–4·12° min^{-1}; three standard reflections measured every 7200 s (no changes); 1514 observed reflections on the basis $I \geq 3\sigma(I)$; Lorentz and polarization correction and empirical absorption correction, based on ψ scan (North, Phillips & Mathews, 1968) (*T* factor: 0·96–0·99). The structure was solved by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}0068|F_o|^2]^{-1}$; complex neutral scattering factors from *International Tables for X-ray Crystallography* (1974). All non-H atoms were refined anisotropically. H atoms belonging to C(6) and C(7) were fixed in calculated positions (C—H = 1·0 Å; $B_H = B_C + 1{\cdot}0$ Å^2) and allowed to ride on the atoms to which they were bonded. The remaining H atoms were treated as fixed contributors at locations obtained from the difference map ($B_H = B_C + 1{\cdot}0$ Å^2), $R = 0{\cdot}053$ and $wR = 0{\cdot}055$, $S = 0{\cdot}887$; zero weight was assigned to six strong low-order reflections, which may be affected by secondary extinction (101, 042, 003, 204, $\bar{2}14$, $\bar{2}07$); max. shift/e.s.d. = 0·27, max. and min. peaks in final $\Delta\rho$ map 0·9 and $-0{\cdot}8$ e Å^{-3} respectively. Major calculations were carried out on a VAX 11/750 computer using *SHELX*76 system of programs (Sheldrick, 1976) and *ORTEP* plotting program (Johnson, 1965).

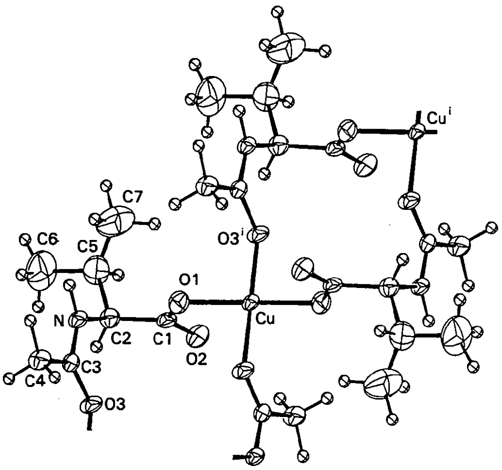

Fig. 1. *ORTEP* view of $[Cu(C_7H_{12}NO_3)_2]_n$ showing the atom numbering and thermal ellipsoids (40%) for the non-H atoms. The H atoms are represented as spheres of arbitrary radius.

Table 1. *Final positional and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cu	0·0	0·0	0·0	1·81 (3)
O(1)	0·1344 (4)	−0·1709 (4)	0·0949 (2)	2·5 (1)
O(2)	−0·2133 (5)	−0·2229 (5)	0·1763 (3)	3·3 (1)
C(1)	−0·0052 (6)	−0·2500 (5)	0·1652 (3)	2·1 (1)
C(2)	0·1079 (7)	−0·3791 (6)	0·2425 (3)	2·1 (1)
N	0·3108 (5)	−0·4717 (5)	0·1958 (2)	2·0 (1)
C(3)	0·2820 (6)	−0·6453 (5)	0·1264 (3)	2·0 (1)
O(3)	0·0767 (4)	−0·7395 (4)	0·1010 (2)	1·9 (1)
C(4)	0·4997 (6)	−0·7253 (6)	0·0797 (3)	2·7 (1)
C(5)	0·180 (1)	−0·2385 (9)	0·3482 (4)	4·8 (2)
C(6)	0·278 (2)	−0·373 (1)	0·4253 (5)	7·4 (3)
C(7)	0·321 (2)	−0·031 (1)	0·3390 (6)	6·8 (3)

Table 2. *Bond distances* (Å) *and bond angles* (°)

Cu—O(1)	1·908 (3)	N—C(3)	1·316 (4)
Cu—O(3ⁱ)	1·962 (2)	C(3)—O(3)	1·255 (4)
C(1)—O(1)	1·275 (4)	C(3)—C(4)	1·500 (5)
C(1)—O(2)	1·226 (5)	C(2)—C(5)	1·547 (6)
C(1)—C(2)	1·523 (6)	C(5)—C(6)	1·502 (10)
C(2)—N	1·462 (5)	C(5)—C(7)	1·431 (9)
O(1)—Cu—O(3ⁱ)	90·4 (1)	C(2)—N—C(3)	121·6 (3)
O(1)—Cu—O(3ⁱⁱ)	89·6 (1)	N—C(3)—O(3)	120·1 (3)
O(1)—C(1)—O(2)	125·3 (4)	N—C(3)—C(4)	118·2 (3)
O(1)—C(1)—C(2)	114·9 (3)	O(3)—C(3)—C(4)	121·7 (3)
O(2)—C(1)—C(2)	119·7 (4)	C(2)—C(5)—C(6)	110·3 (4)
C(1)—C(2)—N	111·9 (3)	C(2)—C(5)—C(7)	116·0 (5)
N—C(2)—C(5)	110·9 (4)	C(6)—C(5)—C(7)	114·2 (6)
C(1)—C(2)—C(5)	111·3 (3)		

Symmetry code: (i) $x, y+1, z$; (ii) $-x, -1-y, -z$.

Final positional parameters for non-H atoms are given in Table 1.*

Discussion. Bond distances and angles are given in Table 2 with atom numbering as in Fig. 1.

The structure is made up of polymeric ribbons running along the *b* axis. Each acetyl-DL-valinate ion bridges two Cu atoms, *b* Å away from each other, through one carboxylic O and the peptidic O. Each Cu atom lies on a symmetry center and shows a square-planar geometry confirming the previous suggestion from the electronic spectrum. The second carboxylic O is 2·904 (4) Å from the Cu in an out-of-plane position with an angle between the Cu—O(2) vector and the normal to the coordination plane of 40·3 (1)°.

In this case, the formation of the anhydrous species probably activates the coordination of the peptidic O, while it is excluded in other binary and ternary complexes by the presence of much stronger donors

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51298 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

such as water and amine molecules (Antolini, Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue, Pellacani & Saladini, 1982; Antolini, Menabue, Saladini, Sola, Battaglia & Bonamartini Corradi, 1984). The coordination of peptidic O is not usual and is observed in few instances for square-pyramidal copper(II) complexes with peptides (Dehand, Jordanov, Keck, Mosset, Bonnet & Galy, 1979; Freeman, Healy & Scudder, 1977; Freeman, Robinson & Schoone, 1964; Franks & van der Helm, 1971).

In the ligand, the peptide oxygen–metal coordination causes a significant lengthening of the C(3)—O(3) distance with respect to other $\mathrm{Cu^{II}}$ *N*-acetyl amino acidates, but the peptide group remains strictly planar. The remaining distances and angles within the *N*-acetyl-DL-valinate moiety are consistent with those found in previously cited $\mathrm{Cu^{II}}$ complexes.

The presence of hydrogen bonding involving the uncoordinated carboxylic O and amide N

N–H(2)	N···O(2^{i})	H(2)···O(2^{i})	N–H(2)···O(2^{i})
0·99 Å	2·936 (4) Å	1·975 Å	162°

[(i) $x+1, y, z$] contributes to crystal packing connecting adjacent chains.

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Chloro(dimethyl sulfide)gold(I)

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Abstract. $[\mathrm{AuCl}(C_2H_6S)]$, $M_r = 294·55$, monoclinic, $P2_1/c$, $a = 6·031\,(1)$, $b = 14·825\,(3)$, $c = 6·417\,(3)$ Å, $\beta = 95·67\,(2)°$, $V = 571·0$ Å^3, $Z = 4$, $D_x = 3·43$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 26·4$ mm^{-1}, $F(000) = 520$, $T = 293$ K. The structure was refined to $R = 0·028$ for 913 observed reflections. The coordination geometry at gold is linear, with Au—S 2·271 (2), Au—Cl 2·288 (2) Å, S—Au—Cl 176·9 (1)°. The molecules are linked into chains by short Au···Au contacts of 3·226 (1) Å, with an Au···Au···Au angle of 168·1 (1)°.

Introduction. Chloro(dimethyl sulfide)gold(I) is an important synthetic intermediate in gold chemistry because the Me_2S ligand is easily replaced. Our attempts to obtain single crystals of Me_2SAuCl were unsuccessful; colourless needles were obtained from a variety of solvent mixtures but were always twinned. The crystal used in this investigation arose from an attempted reaction of Me_2SAuCl with an organic amine. Colourless prisms and tablets were obtained and mounted in glass capillaries.

Experimental. 1657 profile-fitted intensities were measured from $\omega/2\theta$ scans on a Stoe–Siemens four-circle diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50°, quadrant $\pm h+k+l$ and most of the

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