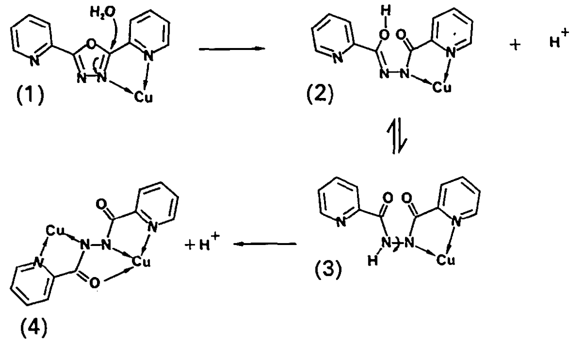
Le mécanisme des principales étapes de cette ouverture est décrit dans le schéma suivant:



La complexation d'un atome de cuivre(II) sur un azote du cycle oxadiazole provoque la fragilisation de l'hétérocycle en induisant un déficit électronique au niveau du carbone lié à cet azote. L'attaque nucléophile d'un molécule d'eau au niveau du carbone déficitaire, suivie de la migration du proton sur l'oxygène de l'oxadiazole provoque la rupture de la liaison carbone–oxygène de l'hétérocycle. Le composé (2) obtenu après perte d'un proton est en équilibre tautomérique avec la forme (3). La libre rotation autour de la liaison N—N et la coordination d'un deuxième atome de cuivre(II) conduit alors au complexe binucléaire (4) objet de l'étude radiocristallographique. Toutes les tentatives de synthèse directe réalisées à partir de la pyridol-2′ pyridinecarbohydrazide conduisent systématiquement à la précipitation du complexe sous forme d'une poudre microcristalline. Seule l'hydrolyse lente du cycle aromatique sous l'effet de la complexation permet la cristallogénèse du complexe binucléaire.

Sa géométrie est décrite par deux plans faisant entre eux un angle de 9,24 (5)° et qui contiennent chacun un Cu^{II}, un cycle pyridine, une molécule d'eau d'hydratation, ainsi qu'un atome de carbone provenant de l'ouverture du cycle oxadiazole. Les atomes contenus dans ces plans sont reliés par la liaison N(2)—N(4); ces deux atomes présentent une hybridation sp^2 déformée comme l'indiquent leurs angles de coordination.

L'atome Cu(1) est en coordination plan carré déformée: deux atomes du ligand N(1), O(2) sont parfaitement coplanaires, mais les atomes N(2) et O(3) sont nettement hors du plan. Par contre, la coordination de Cu(2) est assurée par deux atomes N(3) et N(4) du ligand et par deux molécules d'eau O(4) et O(5), la géométrie plan carré est ici moins déformée.

Deux anions nitrate par unité formulaire assurent l'équilibre des charges; enfin huit molécules d'eau de solvatation, identifiées dans la maille, ne jouent pas de rôle particulier dans la structure.

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Structure of Tetrakis(μ-*N*-chloroacetyl-L-leucinato)-dicopper(II)

By Maninder Singh Hundal,* Sarjit Singh Sandhu and Geeta Sood
Department of Chemistry, Guru Nanak Dev University, Amritsar-143005, India

and Vicky McKie and Santokh Singh Tandon
Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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Abstract. $[Cu(C_8H_{13}ClNO_3)_2]_2$, $M_r = 953.1$, monoclinic, $P2_1$, $a = 13.121$ (4), $b = 13.977$ (5), $c = 13.158$ (5) Å, $\beta = 110.18$ (1)°, $V = 2264.94$ Å^3, $Z = 2$, $D_m = 1.41$ (1), $D_x = 1.40$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 11.76$ cm^{-1}, $F(000) = 988$, $T = 150$ K, $R = 0.058$, $wR = 0.052$ for 2784 reflections with $I > 2.5\sigma(I)$. The title compound has a polymeric structure, each unit of which has four carboxylates

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* Author to whom correspondence should be addressed.

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spanning a Cu—Cu separation of 2·634 (3) Å. The coordination around each Cu^{II} ion is approximately square pyramidal. The axial position is occupied by the carbonyl O atom of the amide group belonging to the symmetry-related *N*-chloroacetyl-L-leucine ligand. The structure is similar to the classic dimeric structure of Cu^{II} acetate monohydrate, but with the axial water replaced by the amide O atom of the neighbouring molecule. The amide O atoms of only two ligands participate in coordination to neighbouring Cu^{II} ions. The other two ligands only coordinate through the carboxylate groups. The mean Cu—O(carboxyl) and Cu—O(peptide) distances are 1·96 (2) and 2·14 (2) Å, respectively.

Introduction. Complexes of *N*-acyl amino acids with metal ions offer the simplest examples for the study of structural features in metal–peptide complexes. It has been observed that in simple amino acids having no side chains, coordination takes place solely through amino and carboxylate groups, thereby forming five- or six-membered chelate rings with the metal ions (Freeman, 1973). Coordination is favoured because of the strongly basic nature of the N atom and the presence of the carboxylate O atom which acts as an anchor during the formation of the chelate ring with the metal ion. Substitution at the amino N atom by groups such as acetyl, benzoyl or benzyloxycarbonyl, decreases the affinity of the amino group for the metal ion. In such cases the coordination takes place only through the carboxylate group. With Cu^{II}, the carboxylate group can act as a non-chelating monodentate, chelating bidentate and bridging bidentate group (Freeman, 1973). The structure determination of the title compound has been undertaken to confirm the existence of the non-chelating coordination of the amide O atom of the *N*-protected amino acid, which ESR and stoichiometric studies had suggested was possible.

Experimental. The complex was prepared by methods reported previously (Sandhu, Hundal, Sood & Dhillon, 1989). D_m was measured by flotation in benzene/bromoform solution. Crystallization was by slow evaporation from a 1:1 mixture of ethanol and water. Bluish-green plate-like crystals appeared after 48 h. The crystal used for data collection had dimensions 0·44 × 0·44 × 0·04 mm. The data were collected at 150 K on a Nicolet *R*3*m* four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). A total of 4251 (3655 independent) reflections ($-15 \leq h \leq 14$, $0 \leq k \leq 16$, $0 \leq l \leq 15$) were measured in the range $4 < 2\theta < 50°$ using a 1·6° ω scan, at a scan rate of 4·5° $\min^{-1}$ and a background-to-scan ratio of 0·1. Cell parameters were determined by least-squares refinement of 21 accurately centred reflections in the range $16 < 2\theta < 30°$. Crystal stability was monitored by recording three standard reflections (300, 060, 004) after every 100 reflections. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied based on ψ-scan data ($T_{\max} = 0{\cdot}980$, $T_{\min} = 0{\cdot}747$).

The structure was solved by the heavy-atom method. The two Cu atoms were located by the Patterson method (*SHELXS*86; Sheldrick, 1986) and the remaining non-H atoms were located by difference Fourier methods using *SHELX*76 (Sheldrick, 1976). The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for all the non-H atoms (*SHELX*76; Sheldrick, 1976). The H atoms were placed at geometrically idealized positions with $U_{\rm iso}$ values fixed at 0·080 Å^2. The refinement of 487 parameters converged to a final $R = 0{\cdot}058$, $wR = 0{\cdot}052$ where $w = (\sigma^2|F_o| + 0{\cdot}000100|F_o|^2)^{-1}$ and $S = 1{\cdot}811$, $(\Delta/\sigma)_{\max} = 0{\cdot}28$. Maximum and minimum heights in the final difference Fourier synthesis were 0·20 and −0·25 e Å^{-3}. Complex neutral-atom scattering factors (Cromer & Liberman, 1970; Cromer & Mann, 1968) were used during all the calculations. The dihedral angles, least-squares planes, hydrogen-bonding geometries and torsion angles were calculated using *PARST* (Nardelli, 1983). The positional parameters of all the atoms are given in Table 1. The important bond lengths, bond angles and torsion angles are given in Table 2.*

Discussion. Fig. 1 shows the structure and the labelling scheme. The complex has a polymeric structure. Each polymeric unit contains two Cu^{II} ions which are bridged by four carboxylate groups. The coordination around each Cu^{II} ion is approximately square pyramidal. The axial position is occupied by the carbonyl O atoms O(35) and O(48) of the amide group belonging to the symmetry-related molecule. A distorted octahedron is completed by another Cu^{II} ion at a distance of 2·634 (3) Å. The structure of each polymeric unit is therefore similar to the classic dimeric structure of Cu^{II} acetate monohydrate (Van Niekerk & Schoening, 1953) except that in the title complex, the axial water has been replaced by the amide O atom of the neighbouring molecule. Participation of the amide O atom in the coordination around the metal ion gives rise to the polymerization in the complex. The amide O atoms of only two ligand molecules participate in the coordination to

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53758 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4) *for the non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.\cos(a_i,a_j).$$

	x	*y*	*z*	U_{eq}
Cu(1)	2025 (2)	2535	423 (2)	124 (6)
Cu(2)	3333 (2)	1152 (2)	282 (2)	118 (6)
O(3)	2091 (4)	1875 (3)	1743 (4)	271 (14)
C(4)	2838 (5)	1243 (4)	2224 (5)	267 (14)
O(5)	3492 (4)	911 (3)	1810 (4)	283 (15)
C(6)	2829 (5)	868 (4)	3277 (5)	288 (16)
N(7)	3958 (4)	920 (3)	4118 (3)	280 (15)
C(8)	4458 (6)	1796 (5)	4458 (7)	366 (16)
O(9)	4026 (4)	2547 (4)	3968 (5)	484 (17)
C(10)	5427 (6)	1722 (5)	5294 (7)	475 (17)
Cl(11)	6498 (2)	2399 (2)	5049 (3)	716 (13)
C(12)	2507 (6)	−161 (3)	3176 (6)	321 (17)
C(13)	1336 (7)	−351 (5)	2369 (6)	470 (16)
C(14)	1167 (7)	−1451 (4)	2219 (6)	486 (16)
C(15)	433 (6)	99 (6)	2661 (8)	699 (16)
O(16)	2126 (4)	3025 (3)	−928 (4)	340 (15)
C(17)	2569 (5)	2452 (5)	−1437 (4)	288 (16)
O(18)	2950 (4)	1688 (3)	−1198 (4)	283 (14)
C(19)	2398 (7)	2846 (5)	−2601 (5)	387 (15)
N(20)	2638 (5)	3893 (4)	−2569 (5)	382 (16)
C(21)	3463 (6)	4236 (5)	−2826 (6)	434 (15)
O(22)	4111 (5)	3769 (4)	−3133 (5)	478 (17)
C(23)	3670 (6)	5318 (5)	−2741 (7)	559 (15)
Cl(24)	2671 (3)	5957 (2)	−2469 (4)	1428 (15)
C(25)	1252 (6)	2522 (7)	−3388 (5)	653 (16)
C(26)	1053 (7)	2943 (6)	−4512 (6)	597 (17)
C(27)	1772 (7)	2509 (6)	−5022 (5)	708 (17)
C(28)	−226 (7)	2556 (9)	−5172 (7)	1649 (16)
O(29)	875 (4)	1677 (3)	−442 (4)	256 (15)
C(30)	1066 (6)	793 (5)	−591 (5)	287 (16)
O(31)	1994 (4)	412 (3)	−237 (4)	256 (15)
C(32)	97 (6)	168 (5)	−1156 (6)	355 (16)
N(33)	443 (5)	−824 (4)	−1151 (5)	375 (17)
C(34)	−39 (5)	−1518 (4)	−838 (5)	221 (15)
O(35)	846 (4)	3580 (3)	541 (4)	269 (15)
C(36)	433 (4)	−2514 (5)	−852 (5)	390 (17)
Cl(37)	1365 (2)	−2611 (2)	−1512 (3)	606 (13)
C(38)	−397 (6)	535 (5)	−2314 (6)	373 (16)
C(39)	−1463 (7)	−30 (5)	−2936 (6)	597 (17)
C(40)	−1720 (7)	254 (6)	−4223 (6)	719 (16)
C(41)	−2398 (6)	206 (6)	−2529 (7)	646 (17)
O(42)	3390 (4)	3257 (3)	1199 (4)	380 (15)
C(43)	4249 (6)	2997 (5)	1039 (5)	306 (17)
O(44)	4431 (4)	2140 (3)	745 (4)	335 (15)
C(45)	5110 (6)	3687 (5)	1225 (6)	365 (16)
N(46)	5713 (5)	3483 (4)	499 (5)	283 (16)
C(47)	5887 (5)	4089 (5)	−191 (6)	283 (14)
O(48)	4281 (4)	−37 (3)	160 (4)	364 (16)
C(49)	6360 (6)	3738 (4)	−1025 (6)	341 (15)
Cl(50)	6416 (3)	2494 (2)	−1147 (3)	703 (13)
C(51)	5902 (7)	3700 (5)	2427 (6)	516 (16)
C(52)	6634 (7)	4599 (6)	2716 (7)	654 (17)
C(53)	5895 (8)	5433 (6)	2853 (8)	1131 (16)
C(54)	7617 (8)	4480 (7)	3568 (8)	1160 (16)

Table 2. *Important bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

Cu(1)—Cu(2)	2·634 (3)	C(8)—O(9)	1·260 (9)
Cu(1)—O(3)	1·942 (6)	C(17)—O(16)	1·301 (9)
Cu(1)—O(16)	1·952 (6)	C(17)—O(18)	1·175 (8)
Cu(1)—O(29)	1·957 (5)	C(21)—O(22)	1·245 (11)
Cu(1)—O(35)	2·171 (5)	C(23)—Cl(24)	1·722 (10)
Cu(1)—O(42)	2·002 (5)	C(30)—O(29)	1·288 (8)
Cu(2)—O(5)	1·977 (6)	C(30)—O(31)	1·262 (9)
Cu(2)—O(18)	1·983 (6)	C(34)—O(35)	1·256 (9)
Cu(2)—O(31)	1·947 (5)	C(36)—Cl(37)	1·733 (8)
Cu(2)—O(44)	1·935 (5)	C(43)—O(42)	1·269 (10)
Cu(2)—O(48)	2·114 (6)	C(43)—O(44)	1·307 (8)
C(4)—O(3)	1·310 (7)	C(49)—Cl(50)	1·751 (6)
C(4)—O(5)	1·254 (9)	C(47)—O(48)	1·244 (10)

O(3)—Cu(1)—Cu(2)	83·4 (2)	O(5)—Cu(2)—Cu(1)	84·1 (2)
O(16)—Cu(1)—Cu(2)	86·7 (2)	O(18)—Cu(2)—Cu(1)	80·9 (2)
O(16)—Cu(1)—O(3)	170·1 (2)	O(18)—Cu(2)—O(5)	164·8 (3)
O(29)—Cu(1)—Cu(2)	84·2 (2)	O(31)—Cu(2)—Cu(1)	83·3 (2)
O(29)—Cu(1)—O(3)	91·0 (2)	O(31)—Cu(2)—O(5)	91·8 (2)
O(29)—Cu(1)—O(16)	88·1 (2)	O(31)—Cu(2)—O(18)	87·9 (2)
O(35)—Cu(1)—O(3)	93·9 (2)	O(44)—Cu(2)—O(5)	89·7 (2)
O(35)—Cu(1)—O(16)	95·9 (2)	O(44)—Cu(2)—O(18)	87·0 (2)
O(35)—Cu(1)—O(29)	91·6 (2)	O(44)—Cu(2)—O(31)	166·5 (3)
O(35)—Cu(1)—Cu(2)	175·0 (2)	O(48)—Cu(2)—Cu(1)	175·4 (2)
O(42)—Cu(1)—Cu(2)	85·2 (2)	O(48)—Cu(2)—O(5)	94·8 (2)
O(42)—Cu(1)—O(3)	91·6 (2)	O(48)—Cu(2)—O(18)	100·3 (2)
O(42)—Cu(1)—O(16)	87·6 (2)	O(48)—Cu(2)—O(31)	92·2 (2)
O(42)—Cu(1)—O(29)	168·7 (2)	O(48)—Cu(2)—O(44)	101·0 (2)
O(42)—Cu(1)—O(35)	99·2 (2)		

N(7)—C(8)—C(10)—Cl(11)	131·3 (6)	N(33)—C(34)—C(36)—Cl(37)	−11·6 (7)
N(20)—C(21)—C(23)—Cl(24)	−7·41 (0)	N(46)—C(47)—C(49)—Cl(50)	10·8 (9)

the neighbouring Cu^{II} ion. The other two ligands coordinate only through the carboxylate groups and the carbonyl O atoms, O(9) and O(22), do not participate in coordination. Out of four *N*-chloroacetyl-L-leucine ligands which are coordinated to two Cu^{II} ions, two behave as bidentate ligands and the other two act as tridentate ligands. This gives rise to linear polymeric chains running parallel to the *a* axis.

The mean-plane calculations show that the Cu^{II} ions are displaced from the mean planes of their four nearest O atoms by 0·18 Å in the case of Cu(1) and 0·24 Å in the case of Cu(2). The two coordination planes Cu(1)–O(29)–C(30)–O(31)–Cu(2)–O(44)–C(43)–O(42) and Cu(1)–O(3)–C(4)–O(5)–Cu(2)–O(18)–C(17)–O(16) are perpendicular to each other; the dihedral angle between them is 90·7 (2)°. The Cu^{II}—O(carboxylate) bond lengths are in full agreement with those found for $[Cu(Ac\text{-}Gly)_2(H_2O)]_2$ (Udupa & Krebs, 1979), $[Cu(Ac\text{-}\beta\text{-}Ala)_2(H_2O)]_2$ (Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1981) and $[Cu(Bz\text{-}\alpha\text{-}Ala)_2(H_2O)]_2$ (Sandhu, Hundal, Sood & Dhillon, 1989). The mean Cu—O(carboxyl) bond length of 1·96 (2) Å is in good agreement with the value of 1·97 (1) Å given by Freeman (1967) for amino acid complexes and lies well within the range 1·89–2·02 Å found in many Cu^{II} carboxylates (Muir, 1973). The Cu—Cu separation [2·634 (3) Å] in this complex is comparable to that found in metallic Cu [2·556 (2) Å] (*International Tables for X-ray Crystallography*, 1962, Vol. III) and in polymeric Cu^{I} acetate [2·544 (4) Å] (Drew, Edwards & Richards, 1973), which indicates that the Cu—Cu interaction is quite strong. This distance is comparable to the 2·616–2·615 Å found in several dimeric Cu^{II} carboxylates (Doedens, 1976).

In the peptide complexes of transition-metal ions the *M*—O(peptide) bonding is often stabilized by the chelation of an adjacent terminal amino group to form a ring (Freeman, 1973) because the O(peptide) is a weak base. Non-chelating *M*—O(peptide) bonding, as observed in the title compound, is very rare. Only one case of a non-chelating *M*—O(peptide) bond [2·237 (3) Å] has been found in Cu(glycine–methionine) (Bear & Freeman, 1976). The Cu—O(peptide) distances in the present case are 2·171 (5) and 2·114 (6) Å, respectively. These distances are slightly longer than the Cu—O(peptide) distances found in the complexes with peptides where O(peptide) acts as a chelating ligand.

The structure of *N*-chloroacetyl-L-leucine is not known so the comparison of torsion angles has been made with L-leucine (Harding & Howieson, 1976) and its Cu^{II} complex (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979). In the solid state L-leucine has the *trans*-N configuration with the bulky side chain *R′* adjacent to the carboxylate group (Fig. 2*a*). In Cu(L-Leu)$_2$ there are two unique ligands, one assumes the *trans*-CO_2 configuration and the second has a *trans*-N configuration (Fig. 2*b*).

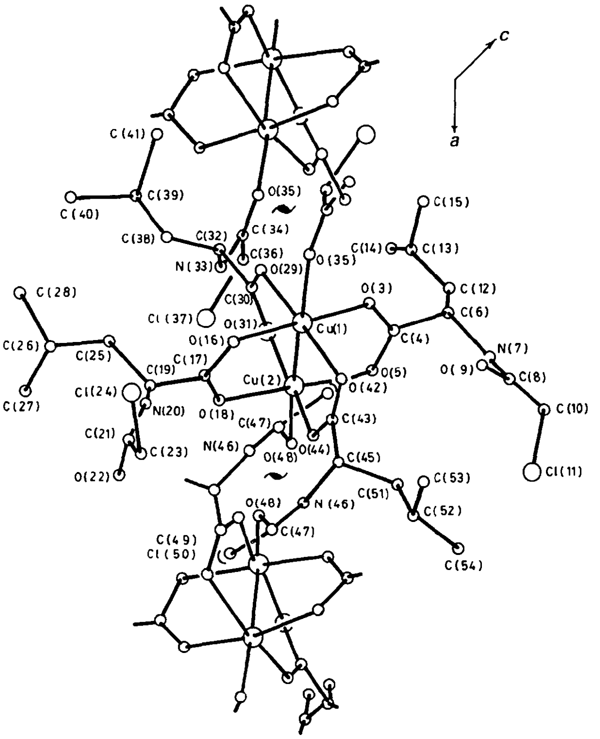
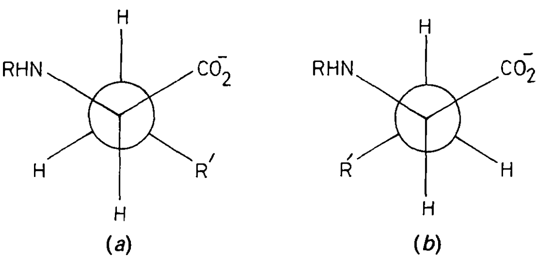


Fig. 1. View of the molecule and two symmetry-related molecules along the *b* axis. For clarity, the complete symmetry-related part has not been drawn.



R = H or $COCH_2Cl$, *R′* = $C(CH_3)_2$

Fig. 2. Newman projection of (*a*) the *trans*-N configuration of the ligand *A* and (*b*) the *trans*-CO_2^- configuration of the ligands *B*, *C* and *D*.

In the present complex, the ligands *B*, *C* and *D* have a *trans*-CO_2 configuration while the ligand *A* has a

With respect to the peptide bond C—N, all four ligands have C_α—N and C—C′ bonds *trans* to each other (where C is the C atom of the peptide group and C′ is the methylene C atom of the acetyl group). This *trans* arrangement is generally considered to be more stable than the *cis* arrangement (Blundell & Johnson, 1976).

The molecule lacks intermolecular hydrogen bonding but intramolecular hydrogen-bonding interactions are formed between the atoms N(20)···Cl(24), N(33)···Cl(37) and N(46)···Cl(50). This intramolecular contact is absent between the atoms N(7) and Cl(11). Examination of the torsion angles explains this missing contact. In ligand *A* the torsion angle N(7)—C(8)—C(10)—Cl(11) is 131·3 (6)°, thereby taking the Cl(11) away from N(7). In the remaining three ligands, C—Cl bonds are almost *cis* to the C—N bonds which brings their respective N and Cl atoms close to each other, resulting in an intramolecular contact.

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