

Fig. 1. Perspective drawing of the structure (Johnson, 1965). Some symmetrically related atoms are also shown. Thermal ellipsoids scaled to 50% probability. For symmetry code see Table 2.

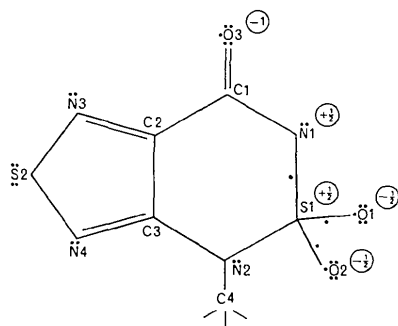


Fig. 2. Major electron distribution model according to Linnett (1966).

Each K^+ ion is surrounded by seven O atoms forming a very distorted laterally capped trigonal prism, with distances ranging from 2.72 (4) to 3.10 (1) Å.

Acta Cryst. (1984). **C40**, 82–85

Structure of (L-Alanyl-L-histidinato)copper(II) 3·5-Hydrate, $[Cu(C_9H_{12}N_4O_3)] \cdot 3 \cdot 5H_2O$

BY Y. MAUGUEN

Laboratoire de Physique, Centre d'Etudes Pharmaceutiques, rue J. B. Clément, 92290 Châtenay-Malabry, France

AND E. VILKAS AND C. AMAR

Laboratoire de Chimie Organique Biologique, Université Paris-Sud, 91405 Orsay, France

(Received 8 February 1983; accepted 19 September 1983)

Abstract. $M_r = 350.82$, orthorhombic, $P2_12_12$, $a = 10.037$ (7), $b = 14.477$ (10), $c = 9.735$ (7) Å, $V = 1414$ Å³, $Z = 4$, $D_x = 1.647$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.43$ mm⁻¹, $F(000) = 727$, room temperature, $R = 0.045$ for 1588 unique observed reflections. The Cu atom is four-coordinated. The four closest

Thanks are given to the CPD del MEC (Spain) for computing time on a Univac 1100 computer. One of us (CEC) acknowledges a research grant given by CSIC, Spain.

References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. D., VAN DEN HARK, TH. E. M. & PRICK, P. A. J. (1980). *DIRDIF. Direct Methods for Difference Structure*. Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands, and Chemistry Department, Univ. of Edinburgh, Scotland.
- CABEZUELO, M. D., CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Acta Cryst.* **B33**, 3598–3601.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982a). *Acta Cryst.* **B38**, 1124–1128.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982b). *Acta Cryst.* **B38**, 1128–1133.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982c). *Acta Cryst.* **B38**, 2296–2298.
- FAYOS, J. & MARTÍNEZ-RIPOLL, M. (1975). *HSEARCH*. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain.
- GARCÍA-MUÑOZ, G., OCHOA, C., STUD, M. & PFLEIDERER, W. (1976). *J. Heterocycl. Chem.* **13**, 793.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LINNETT, J. W. (1966). *The Electron Structures of Molecules. A New Approach*. London: Methuen.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

donor atoms are the amino, peptide and imidazole N atoms of one peptide and a carboxyl O of another. They form an approximate square-planar arrangement around the Cu atom. The Cu atom also interacts weakly with the second O atom of the carboxyl group to which it is bonded. The polymeric Cu–dipeptide–

Cu–dipeptide chains formed are parallel to the crystallographic a axis, and linked by a net of hydrogen bonds involving the water molecules.

Introduction. Histidine is frequently found as part of the active site of metalloproteins. The coordination mode of the metal with histidine-containing peptides has been investigated mainly in solution by potentiometric and spectroscopic methods (Wilson, Kasperian & Martin, 1970; Aiba, Yokoyama & Tanaka, 1974; Agarwal & Perrin, 1975, 1976; Kruck & Sarkar, 1975; Lau & Sarkar, 1981; Ensueque, Demaret & Abello, 1982) and in some cases in the solid state by X-ray analyses (Freeman & Szymanski, 1965; Blount, Fraser, Freeman, Szymanski, Wang & Gurd, 1966; Blount, Fraser, Freeman, Szymanski & Wang, 1967; Österberg, Sjöberg & Söderquist, 1972; Camerman, Camerman & Sarkar, 1976).

Recently, we studied the reactivity of some Cu–histidine-containing dipeptide complexes towards O_2^- produced by the pulse-radiolysis technique. The complexes behave in different ways according to the N or C terminal position of the histidyl residue. The potentiometric and spectroscopic measurements show two different kinds of chelation of the Cu^{2+} ion by the dipeptide (Amar, Vilkas & Foos, 1982).

In this paper we report the crystal structure of one of these complexes, Ala-His– Cu^{2+} , studied by X-ray diffraction.

Experimental. Crystals obtained by mixing equimolar amounts of freshly prepared $Cu(OH)_2$ gel and dipeptide hydrochloride in a 0.2 M NaOH solution; pH of resultant solution adjusted to 7; violet crystals separated on slow evaporation; D_m not determined. Prismatic crystal: $0.1 \times 0.1 \times 0.2$ mm. CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω – 2θ scan technique. Three standard reflections monitored at intervals of 100 measurements: no significant fluctuations. Total of 1802 reflections measured, h 0 to 12, k 0 to 18, l 0 to 12, $2^\circ < \theta < 27.5^\circ$; of these, 1596 with $I > 2\sigma(I)$ considered observed and used in the determination and refinement of the structure. Variances of the intensities, $\sigma^2(I)$, estimated from Poisson counting statistics and from the scatter observed in the three standard reflections. Corrections for Lorentz–polarization effects, but not for absorption. Structure solved by heavy-atom method and Fourier techniques, and refined by full-matrix least-squares methods minimizing $\sum |F_o| - |F_c|^2$. Unit weights for all reflections. Eight reflections clearly in error removed from final calculations. The correctness of the enantiomer has been checked from the known absolute configuration of the amino acids. After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, difference maps clearly indicated H-atom positions. All

H atoms included in the final refinement with isotropic thermal parameters set at 1.2 times the equivalent isotropic value of the corresponding C, N or O atom and with geometrical constraints: C–H 1.08 (riding model), N–H 1.01, O–H 0.97 Å, and H...H 1.54 Å in water molecules, CH_3 as a rigid group. Final R^* 0.045. Mean values of $(|F_o| - |F_c|)^2$ virtually independent of $\sin\theta$ or $|F_o|$. In final cycle $(\Delta/\sigma)_{max}$ and $(\Delta/\sigma)_{ave}$ respectively 0.20 and 0.04 for non-hydrogen atoms. R.m.s. deviation of a reflection of unit weight on an absolute scale of F_c 1.46. In final difference map residual maxima less than $0.4 e \text{ \AA}^{-3}$, except for two peaks (0.9 and $0.6 e \text{ \AA}^{-3}$) near the Cu atom. No correction for secondary extinction. Scattering factors for neutral atoms and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Most of the calculations performed with *SHELX76* (Sheldrick, 1976).

Discussion. Final positional and equivalent isotropic thermal parameters for non-hydrogen atoms are in Table 1, interatomic distances and angles in Table 2. A view of the molecule, with the numbering scheme is shown in Fig. 1.

The Cu atom is involved in square-planar coordination and is situated at the center of the plane defined by N(1), N(2), N(3) and O(3¹). The Cu–ligand lengths agree well with those found in other similar complexes in which the N peptide atom is shared by a five- and six-membered ring (de Meester & Hodgson, 1977, 1976; Camerman, Camerman & Sarkar, 1976; Freeman & Szymanski, 1967), except for the Cu–N(2) bond which lies at the limit of the normal range and is shorter in the present structure: 1.933 (5) Å instead of 1.951 (3), 1.950 (4), 1.960 (3), 1.952 (7) Å respectively. The deviations of N(1), N(2), N(3) and O(3¹) from their plane of best fit are between +0.09 and –0.09 Å and such that the configuration of these four atoms is a very flattened tetrahedron. The Cu atom is 0.05 Å out of the plane. The same trend has been reported for Cu^{II} complexes of glycyl-L-histidine (Blount *et al.*, 1966, 1967) and for (glycyl-L-histidylglycinato)copper(II) (de Meester & Hodgson, 1977).

The second O atom O(2¹) of the coordinated carboxyl group also interacts weakly with the Cu atom, at a longer distance of 2.527 (5) Å. The line Cu...O(2¹) is severely displaced from the normal square-pyramidal geometry, the angles O(2¹)–Cu–X ranging from 55.4 to 121.0°. A similar geometry is found in the structure of copper glutamate (Gramaccioli & Marsh, 1966).

* Lists of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38875 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) of the non-hydrogen atoms

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu	558 (1)	3124 (1)	5338 (1)	19.3 (3)
N(1)	1570 (6)	2883 (4)	7057 (6)	28 (3)
C(1)	1488 (8)	3869 (7)	9134 (8)	51 (5)
C(2)	794 (7)	3126 (6)	8299 (6)	33 (3)
C(3)	-601 (8)	3461 (4)	7886 (6)	23 (3)
O(1)	-1433 (6)	3631 (5)	8829 (5)	40 (3)
N(2)	-822 (5)	3558 (4)	6564 (5)	17 (2)
C(4)	-2070 (6)	3974 (4)	6130 (6)	20 (3)
C(5)	-3101 (6)	3269 (5)	5643 (6)	23 (3)
O(2)	-4148 (4)	3580 (4)	5143 (5)	38 (3)
O(3)	-2900 (5)	2430 (3)	5745 (5)	30 (3)
C(6)	-1821 (6)	4662 (4)	4981 (6)	22 (3)
C(7)	-1363 (6)	4212 (4)	3698 (6)	20 (3)
N(3)	-370 (6)	3550 (4)	3704 (5)	23 (3)
C(8)	-238 (6)	3268 (5)	2416 (6)	27 (3)
N(4)	-1057 (6)	3713 (5)	1613 (5)	31 (3)
C(9)	-1790 (8)	4321 (6)	2390 (7)	33 (4)
W(1)	-4164 (6)	3693 (5)	9150 (7)	55 (4)
W(2)	3899 (6)	4080 (5)	7047 (6)	54 (4)
W(3)	-6006 (7)	3797 (5)	3021 (6)	57 (4)
W(4)	0	0	8893 (8)	51 (5)

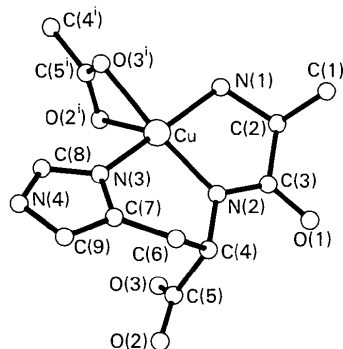


Fig. 1. The molecular structure of the (L-alanyl-L-histidinato)-copper(II) complex showing the atom numbering.

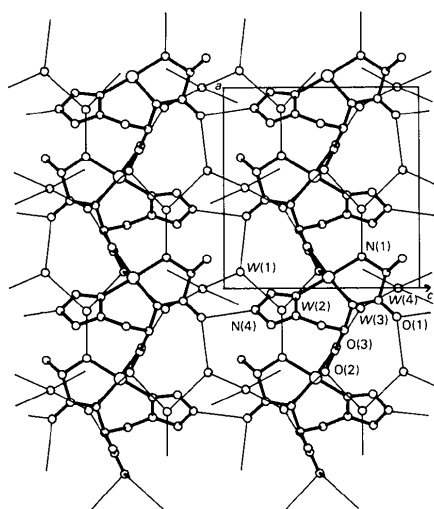


Fig. 2. Molecular packing viewed along *b*.

This structural assignment supports the conclusion drawn from the solution data (Amar *et al.*, 1982; Huet & Vilkas, unpublished results), namely that at pH 6–8 the predominant species is a 1:1 complex in which the Cu^{2+} ion is coordinated to the deprotonated ligand through three N donor atoms belonging to the amino, peptide and imidazole groups respectively.

Within the dipeptide, bond distances and angles are normal and in good agreement with those found in related structures; there are, however, some small deviations from planarity in the peptide group C(2), C(3), O(1), N(2), C(4) (mean deviation 0.04, maximum 0.057 Å), the position of N(2) probably being affected by residual peaks around the Cu atom. In the imidazole ring, which is quite planar, we observed a pronounced double character of the bonds C(8)–N(3) [1.326 (7) Å] and C(8)–N(4) [1.305 (9) Å], already noticed by de Meester & Hodgson (1977) in the structure of (glycyl-L-histidyl-glycinato)copper(II).

The packing of the molecules is illustrated in Fig. 2. The structure is organized as chains of dipeptides connected *via* the Cu atoms. These chains are arranged in layers by a complex network of hydrogen bonds, listed in Table 2. These layers are hydrogen bonded through the water molecule W(4) lying on the twofold axis.

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

Cu–N(1)	1.989 (6)	Cu–O(3 ⁱ)	2.038 (5)
Cu–N(2)	1.933 (5)	Cu–O(2 ⁱ)	2.527 (5)
Cu–N(3)	1.944 (5)		
N(1)–C(2)	1.480 (8)	C(5)–O(3)	1.237 (8)
C(2)–C(1)	1.517 (12)	C(4)–C(6)	1.519 (8)
C(2)–C(3)	1.535 (10)	C(6)–C(7)	1.482 (8)
C(3)–O(1)	1.265 (8)	C(7)–N(3)	1.382 (8)
C(3)–N(2)	1.314 (7)	N(3)–C(8)	1.326 (7)
N(2)–C(4)	1.453 (8)	C(8)–N(4)	1.305 (9)
C(4)–C(5)	1.528 (9)	N(4)–C(9)	1.373 (10)
C(5)–O(2)	1.242 (8)	C(9)–C(7)	1.353 (9)
N(1)–Cu–N(2)	84.5 (2)	N(2)–Cu–O(2 ⁱ)	121.0 (2)
N(1)–Cu–N(3)	171.5 (2)	N(2)–Cu–O(3 ⁱ)	172.6 (2)
N(1)–Cu–O(2 ⁱ)	85.7 (2)	N(3)–Cu–O(2 ⁱ)	102.4 (2)
N(1)–Cu–O(3 ⁱ)	88.8 (2)	N(3)–Cu–O(3 ⁱ)	93.7 (2)
N(2)–Cu–N(3)	93.4 (2)	O(2 ⁱ)–Cu–O(3 ⁱ)	55.4 (2)
Cu–N(1)–C(2)	112.1 (4)	C(4)–C(5)–O(3)	116.9 (6)
N(1)–C(2)–C(1)	111.4 (6)	C(4)–C(5)–O(2)	121.3 (6)
N(1)–C(2)–C(3)	110.0 (5)	O(2)–C(5)–O(3)	121.7 (6)
C(1)–C(2)–C(3)	109.6 (7)	C(4)–C(6)–C(7)	112.5 (5)
C(2)–C(3)–N(2)	116.4 (6)	C(6)–C(7)–N(3)	121.7 (5)
C(2)–C(3)–O(1)	118.3 (5)	C(6)–C(7)–C(9)	130.1 (6)
O(1)–C(3)–N(2)	125.3 (7)	N(3)–C(7)–C(9)	108.2 (6)
C(3)–N(2)–Cu	116.7 (5)	C(7)–N(3)–Cu	124.7 (4)
C(4)–N(2)–Cu	124.9 (4)	C(7)–N(3)–C(8)	106.4 (5)
N(2)–C(4)–C(6)	110.1 (5)	N(3)–C(8)–N(4)	110.5 (6)
N(2)–C(4)–C(5)	113.4 (5)	C(8)–N(4)–C(9)	109.0 (6)
C(6)–C(4)–C(5)	108.7 (5)	N(4)–C(9)–C(7)	105.9 (6)
Hydrogen bonds			
N(4)–H...O(1 ⁱⁱ)	2.740 (7)	W(3)–H...O(3 ^v)	2.865 (8)
W(1)–H...W(4 ⁱⁱⁱ)	2.813 (8)	W(3)–H...O(2)	2.800 (8)
W(1)–H...O(1)	2.761 (8)	W(4)–H...W(3 ^{iv})	2.743 (9)
W(2)–H...O(2 ^{iv})	2.793 (8)	N(1)–H...W(2)	2.910 (9)
W(2)–H...W(1 ^v)	2.878 (9)		

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $x, y, z - 1$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 2 - z$; (iv) $1 + x, y, z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

References

- AGARWAL, R. P. & PERRIN, D. D. (1975). *J. Chem. Soc. Dalton Trans.* pp. 268–272.
- AGARWAL, R. P. & PERRIN, D. D. (1976). *J. Chem. Soc. Dalton Trans.* pp. 89–92.
- AIBA, H., YOKOYAMA, A. & TANAKA, H. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1437–1441.
- AMAR, C., VILKAS, E. & FOOS, J. (1982). *J. Inorg. Biochem.* **17**, 313–323.
- BLOUNT, J. F., FRASER, K. A., FREEMAN, H. C., SZYMANSKI, J. T. & WANG, C. H. (1967). *Acta Cryst.* **22**, 396–405.
- BLOUNT, J. F., FRASER, K. A., FREEMAN, H. C., SZYMANSKI, J. T., WANG, C. H. & GURD, F. R. N. (1966). *J. Chem. Soc. Chem. Commun.* pp. 23–24.
- CAMERMAN, N., CAMERMAN, A. & SARKAR, B. (1976). *Can. J. Chem.* **54**, 1309–1316.
- ENSUQUE, A., DEMARET, A. & ABELLO, L. (1982). *J. Chim. Phys.* **79**, 185–188.
- FREEMAN, H. C. & SZYMANSKI, J. T. (1965). *J. Chem. Soc. Chem. Commun.* pp. 598–599.
- FREEMAN, H. C. & SZYMANSKI, J. T. (1967). *Acta Cryst.* **22**, 406–417.
- GRAMACCIOLI, C. M. & MARSH, R. E. (1966). *Acta Cryst.* **21**, 594–600.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KRUCK, T. P. A. & SARKAR, B. (1975). *Inorg. Chem.* **14**, 2383–2388.
- LAU, S. & SARKAR, B. (1981). *J. Chem. Soc. Dalton Trans.* pp. 491–494.
- MEESTER, P. DE & HODGSON, D. J. (1976). *J. Am. Chem. Soc.* **98**, 7086–7087.
- MEESTER, P. DE & HODGSON, D. J. (1977). *Acta Cryst.* **B33**, 3505–3510.
- ÖSTERBERG, R., SJÖBERG, B. & SÖDERQUIST, U. (1972). *J. Chem. Soc. Chem. Commun.* pp. 983–985.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WILSON, E. W. JR, KASPERIAN, M. H. & MARTIN, P. B. (1970). *J. Am. Chem. Soc.* **92**, 5365–5372.

Acta Cryst. (1984). **C40**, 85–87

**Structure of *cis*-Bis(2,2'-bipyridine)bis(benzenethiolato)nickel(II) Dideuteriohydrate,
[Ni(C₁₀H₈N₂)₂(C₆H₅S)₂].D₂O**

BY KOHTARO OSAKADA, TAKAKAZU YAMAMOTO* AND AKIO YAMAMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

AND AKIO TAKENAKA AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

(Received 20 June 1983; accepted 30 September 1983)

Abstract. $M_r = 609.44$, monoclinic, $P2_1/n$, $a = 15.999$ (2), $b = 12.421$ (1), $c = 15.343$ (2) Å, $\beta = 106.61$ (1)°, $V = 2921.6$ (6) Å³, $Z = 4$, $D_x = 1.385$, $D_m = 1.361$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu(\text{Cu } K\alpha) = 17.7$ cm⁻¹, $F(000) = 816$, room temperature. $R = 0.077$ for 3973 observed reflections. The Ni^{II} coordination is a distorted octahedron with two chelating bipyridine ligands and two thiophenolate anions. The complex has approximate 2 (C_2) symmetry. Hydrogen bonding between an S atom and the D₂O molecule is observed, the S...O distance being 3.220 (8) Å.

Introduction. The title compound was prepared from the reaction of bis(1,5-cyclooctadiene)nickel with diphenyl disulfide, PhSSPh, in the presence of bipyridine. The most plausible structure of the compound deduced from its chemical and spectroscopic analyses is an

octahedral one around a Ni^{II} center with two thiophenolate ligands which are formed by cleavage of the S—S bond in the reactant. However, the structure of complexes of the type NiX₂(bpy)₂ ($X = \text{Cl, Br, etc.}$) has not been confirmed by X-ray study, as the 20-electron configuration is not as common in nickel complexes. An alternative configuration around a nickel(0) center with a neutral non-cleaved diphenyl disulfide ligand cannot be excluded for the compound. Analytical and spectroscopic data do not give a definite conclusion. Thus the crystals have been subjected to X-ray analysis, and the structure of the bis(benzenethiolato) complex formed by the S—S bond cleavage has been unequivocally confirmed.

Experimental. Dark-brown prisms (from a mixture of methanol-d₄ and D₂O), 0.5 × 0.5 × 0.3 mm, Rigaku automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, unit-cell dimensions by

* To whom correspondence should be addressed.