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The Crystal and Molecular Structure of the Copper(II) Chelate of L-Leucyl-L-tyrosine

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The crystal structure of the title compound, $[Cu(C_{15}H_{20}N_2O_4) (H_2O)].2H_2O.C_2H_5OH$, has been determined and refined by three-dimensional least-squares techniques. The crystals are orthorhombic, space group $P2_12_12_1$, $Z=4$, with $a=15\cdot545$ (1), $b=16\cdot121$ (2) and $c=8\cdot6838$ (5) Å. Diffractometer intensity data were collected for all unique reflections with $\theta < 75°$, using Ni-filtered Cu $K\alpha$ radiation. The final $R=3\cdot5\%$ for all 2546 data. The estimated standard deviations are between 0·003 and 0·007 Å for all C, N and O atoms. The coordination of the copper(II) ion is best described as square pyrimidal. Polymer-like chains are formed in the solid state by the bridging of copper(II) ions with the terminal carboxyl groups in a direction parallel to the twofold screw axis in the **c** direction. Hydrogen bonds involving the water molecules, ethanol molecule and the peptide join the chains largely in the **a** direction.

Introduction

As part of a general study of the influence of transition metal cations on the conformation of amino acids and peptides we have determined the crystal structure of the copper(II) chelate of L-leucyl-L-tyrosine (CULT). Previously it has been reported that an interaction occurs between the Cu^{2+} ion and the activated aromatic ring of the tyrosine residue in the copper(II) chelates of both glycyl-L-leucycl-L-tyrosine (Franks & Van der Helm, 1971) and L-tyrosine (Van der Helm & Tatsch, 1972). It was, therefore, of interest to ascertain the position of the tyrosine side chain of CULT with respect to the Cu^{2+} ion. It was determined that although the conformations of the side chains were approximately the same for all three structures, a close contact was not observed in CULT. This interaction takes on added significance when one considers these molecules as possible model compounds for the active site in copper containing oxidases. Because activated

aromatic rings are often substrates for these enzymes one might suggest that bonding at the active site, with subsequent electron transfer, takes place through the π-electrons of the aromatic ring.

The purpose of this communication is to present the description of the structure of CULT and to compare this structure to those in which an interaction has been observed.

Experimental

The compound CULT was prepared by reacting L-leucyl-L-tyrosine, copper sulfate and barium hydroxide in molar proportions of 1:1:1. The precipitate of barium sulfate was removed by centrifugation. The resulting solution was approximately 0·05 M in concentration of complex. The solution was then diluted with an equal volume of ethanol and after a few hours deep-blue needles crystallized from solution. These crystals were redissolved in water and a few drops of ethanol were added each day for several days. After three days deep-blue plates crystallized from the solution. The plate face is the (100) plane while the crystals are elongated along the **c** axis. During collection of

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data it was noted that slow decomposition took place. In addition the extinction, using polarized light, of the crystal lying on its plate face was initially sharp but became quite broad after two or three weeks.

Crystallographic data (Table 1) and integrated X-ray intensities were collected at room temperature using a Nonius CAD4 automatic diffractometer. A total of 2546 data, comprising all unique reflections with $2\theta \leq 150°$, were collected using a freshly recrystallized crystal with dimensions $0.09 \times 0.03 \times 0.7$ mm. Data was collected using Ni-filtered Cu $K\alpha$ radiation and θ–2θ scans. The θ scan width was calculated as $1.0 + 0.1 \tan \theta$. A total of 40s were spent scanning the peak with 10s each being used for scanning the high-θ and the low-θ background. A total of 172 reflections were considered indistinguishable from the background, having $I < 1.4\sigma(I)$. For the purpose of least-squares refinement these reflections were assigned a value equal to 1.0 times the square root of the total count. The decomposition mentioned previously amounted to 35% at the end of data collection. The decomposition appeared to be isotropic and was corrected for by scaling with the monitor reflections. The decomposition did not affect the mosaic of the crystal during the data collection. After the solution of the structure the decomposition was attributed to the loss of ethanol. Lorentz, polarization and absorption corrections were applied ($\mu = 18.3$ cm^{-1}). For the absorption correction, the program of Coppens, Leiserowitz & Rabinovich (1965) was used. This program uses the numerical integration method of Gauss and in this case eight sampling points were used along each axis.

Structure determination and refinement

The position of the copper atom was obtained from the three Harker sections of a sharpened Patterson synthesis. After two cycles of least-squares refinement the $R = (\sum \|kF_o| - |F_c\|/\sum|kF_o|)$ was 0.44. A difference Fourier map was then calculated from which the positions of 19 nonhydrogen atoms were located. After three more cycles R was 0.24. At this point a difference Fourier was calculated from which the remaining nonhydrogen atoms, including two water molecules and an ethanol molecule of solvation, were located. The nonhydrogen atoms were given anisotropic temperature factors and the observed structure

Table 1. Crystallographic data

Formula: [Cu(C$_{15}$H$_{20}$N$_2$O$_4$) (H$_2$O)].2H$_2$O.C$_2$H$_5$OH
F.W. 455·99   Space group: $P2_12_12_1$
Systematic absences: $h00$, $h = 2n + 1$ $a = 15.545 \pm 0.001$ Å
                     $0k0$, $k = 2n + 1$ $b = 16.121 \pm 0.002$
                     $00l$, $l = 2n + 1$ $c = 8.6838 \pm 0.0005$
(determined by least-squares fit to the $+2\theta$ and -2θ values of 52 reflections)
$V = 2176.2$ Å^3 $D_c = 1.394$ g cm^{-3}
$Z = 4$ $D_o = 1.392$ g cm^{-3}
$F(000) = 964$ (measured by flotation in CCl$_4$/C$_6$H$_{12}$ mixture)

factors were corrected for the anomalous dispersion of copper (Patterson, 1963). After several more cycles of least-squares refinement a difference Fourier was calculated from which the positions of all hydrogen atoms were located. Least-squares refinement of the nonhydrogen atoms, using anisotropic temperature factors, and hydrogen atoms, using isotropic temperature factors, was terminated when all shifts for the nonhydrogen atom parameters were less than the corresponding estimated standard deviation. It may be noted that the two hydrogen atoms on the terminal NH$_2$ group were fixed at the positions calculated from geometrical considerations. These positions correspond to peaks in the difference Fourier of 0.40 and 0.36 e Å^{-3}. During refinement the positional parameters of these two atoms showed unreasonable shifts and for this reason were not allowed to vary. The most pronounced features in a final difference Fourier were two peaks of 0.5 and 0.6 e Å^{-3}, located at a distance of 1.4 Å from the Cu^{+2} ion.

All least-squares refinement was carried out by the block-diagonal least-squares program of Ahmed (1966). The unweighted R based on final parameters (Tables 2, 3 and 4) is 0.035 for all data. The atomic scattering factors for Cu^{2+}, N, C, O and the anomalous scattering factors for Cu^{2+} were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for hydrogen atoms were those of Stewart, Davidson & Simpson (1965). A weighting scheme was used which assigns an experimental weight to each structure factor as defined below:

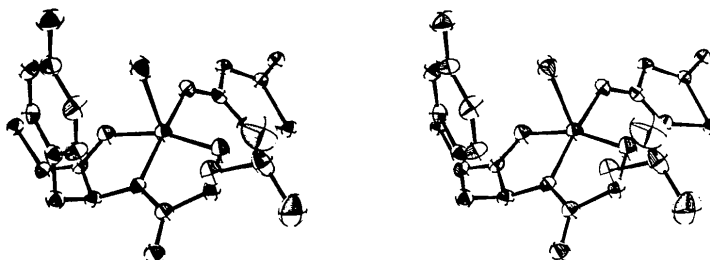$$w'_F = \frac{1}{\sigma_F^2}$$

where

Fig. 1. Stereo view (Johnson, 1965) of a single molecule.

$$\sigma_F = \tfrac{1}{2}\left[\frac{\sigma^2+(0\cdot05P)^2}{(P)(\text{Lp})}\right]^{1/2}$$

in which $\sigma = T^{1/2}v$, $v =$ scan speed, $T = \text{Pk} + 2(R+L)$, $P = [\text{Pk} - 2(R+L)]v$, $R =$ right background, $L =$ left background, Lp $=$ Lorentz and polarization corrections. In the structure-factor analysis the average values of $w_F \Delta F^2$ did not show a significant variation with either $|F_o|$ or $\sin\theta/\lambda$, validating the weighting scheme which was used.*

Table 2. *Positional parameters of copper, carbon, nitrogen and oxygen atoms*

Calculated standard deviations for the last digit are listed in parentheses.

	x	y	z
Cu²⁺	0·76326 (3)	0·08295 (2)	0·17368 (5)
C(1)	0·8788 (2)	0·2042 (2)	0·0401 (5)
C(2)	0·9171 (2)	0·1708 (2)	0·1893 (5)
C(3)	0·8892 (2)	0·0853 (2)	0·4147 (4)
C(4)	0·8221 (2)	0·0199 (2)	0·4518 (4)
C(5)	0·8529 (3)	0·2955 (2)	0·0654 (5)
C(6)	0·8376 (3)	0·3450 (2)	−0·0829 (6)
C(7)	0·7939 (4)	0·4274 (3)	−0·0442 (8)
C(8)	0·9212 (4)	0·3609 (3)	−0·1685 (8)
C(9)	0·8938 (2)	0·1512 (2)	0·5454 (4)
C(10)	0·8149 (2)	0·2058 (2)	0·5529 (4)
C(11)	0·7394 (2)	0·1804 (2)	0·6230 (4)
C(12)	0·6679 (2)	0·2318 (2)	0·6312 (5)
C(13)	0·6716 (2)	0·3107 (2)	0·5666 (5)
C(14)	0·7456 (3)	0·3365 (2)	0·4928 (5)
C(15)	0·8168 (2)	0·2846 (2)	0·4865 (5)
C(16)	0·9602 (4)	−0·0447 (4)	0·0131 (9)
C(17)	1·0396 (5)	−0·0175 (4)	0·0939 (8)
N(1)	0·8013 (2)	0·1544 (2)	−0·0026 (4)
N(2)	0·8673 (2)	0·1207 (2)	0·2676 (4)
O(1)	0·9920 (2)	0·1946 (2)	0·2270 (4)
O(2)	0·8293 (2)	−0·0178 (2)	0·5778 (3)
O(3)	0·7611 (2)	0·0075 (2)	0·3571 (3)
O(4)	0·6518 (2)	0·1619 (2)	0·2646 (4)
O(5)	0·6030 (2)	0·3639 (2)	0·5709 (4)
O(6)	0·9452 (2)	0·0060 (2)	−0·1189 (5)
O(7)	1·1151 (2)	0·2305 (2)	−0·0237 (5)
O(8)	1·0823 (3)	0·1031 (3)	−0·2307 (5)

Description and discussion of the structure

A stereoview of the molecule is shown in Fig. 1. As mentioned above, one of the primary purposes of determining this structure was to ascertain the position of the aromatic ring with respect to the copper(II) ion. It can be seen that the side chain swings up and in towards the copper(II) ion. The closest contact, however, is 3·926 Å between Cu²⁺ and C(11). The two five-membered chelate rings are formed by using the terminal $-NH_2$ group, the peptide-group nitrogen and one oxygen atom of the carboxyl group. This type of chelation is most often found for dipeptides in which a

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30776 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Anisotropic temperature factor parameters of copper, carbon, nitrogen and oxygen atoms*

The anisotropic temperature factors are expressed as exp [−$(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$]. The parameters are multiplied by 10^4. Standard deviations for the last digit in parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu²⁺	23·2 (1)	19·3 (1)	68·5 (5)	−11·7 (2)	−8·1 (6)	1·3 (5)
C(1)	31 (2)	23 (1)	68 (5)	−16 (2)	−2 (5)	8 (4)
C(2)	25 (1)	19 (1)	78 (5)	−11 (2)	−7 (5)	10 (4)
C(3)	18 (1)	17 (1)	73 (5)	−4 (2)	3 (4)	12 (4)
C(4)	19 (1)	19 (1)	67 (5)	−3 (2)	15 (4)	1 (4)
C(5)	40 (2)	22 (1)	93 (6)	−5 (3)	−17 (6)	1 (5)
C(6)	47 (2)	26 (1)	117 (7)	−10 (3)	−43 (7)	30 (5)
C(7)	78 (3)	35 (2)	253 (12)	23 (4)	−27 (11)	48 (9)
C(8)	65 (3)	49 (2)	177 (10)	−14 (4)	22 (11)	73 (9)
C(9)	24 (1)	22 (1)	72 (5)	0 (2)	−6 (4)	−6 (4)
C(10)	24 (1)	21 (1)	64 (5)	−1 (2)	−9 (4)	−15 (4)
C(11)	29 (1)	21 (1)	74 (4)	0 (2)	2 (5)	0 (4)
C(12)	26 (1)	25 (1)	85 (6)	−4 (2)	17 (4)	0 (4)
C(13)	28 (1)	25 (1)	94 (6)	9 (2)	1 (5)	−5 (5)
C(14)	34 (2)	22 (1)	122 (6)	3 (2)	30 (6)	21 (5)
C(15)	28 (2)	25 (1)	108 (6)	−7 (2)	14 (5)	8 (5)
C(16)	69 (3)	45 (2)	291 (15)	−20 (5)	90 (13)	−43 (11)
C(17)	82 (4)	53 (3)	226 (12)	24 (6)	−4 (13)	−29 (11)
N(1)	42 (2)	31 (1)	73 (5)	−32 (2)	−20 (5)	14 (5)
N(2)	21 (1)	20 (1)	62 (4)	−8 (2)	−2 (4)	11 (3)
O(1)	26 (1)	36 (1)	97 (4)	−23 (2)	−12 (3)	30 (4)
O(2)	24 (1)	26 (1)	73 (4)	−14 (2)	2 (3)	26 (3)
O(3)	28 (1)	24 (1)	85 (4)	−19 (2)	−12 (4)	15 (3)
O(4)	47 (2)	40 (1)	110 (5)	24 (2)	−27 (5)	−31 (4)
O(5)	32 (1)	34 (1)	142 (5)	23 (2)	24 (4)	22 (4)
O(6)	44 (2)	61 (2)	217 (8)	−23 (3)	−5 (6)	−24 (7)
O(7)	54 (2)	56 (2)	148 (6)	−22 (3)	42 (6)	15 (6)
O(8)	68 (2)	73 (2)	155 (6)	−48 (4)	2 (6)	6 (7)

histidine residue is not involved. For example, this chelation is found in the copper(II) chelates of both glycylglycine (Strandberg, Lindqvist & Rosenstein, 1961) and glycyl-L-tryptophan (Hursthouse, Jayaweera, Milburn & Quick, 1971). The coordination sphere of copper(II) ion is seen to be square pyramidal. A water molecule occupies the apical position of the square pyramid.

Bond distances and numbering scheme are given in Fig. 2 and bond angles are given in Fig. 3. In addition the average values for bond distances in several copper chelates as compiled by Freeman (1967) are given in Fig. 4 along with the values reported for this structure. No significant differences with previous observations were found although the value of 2·291 Å for the copper to apical oxygen atom compares with the shortest distance of the large range of values compiled by Freeman. The expectedly short value of 1·909 Å for the copper to peptide N distance is due to increased attraction of the ionized nitrogen.

Two bond distances in the peptide group are changed significantly from the free peptide. They are the C(2)–N(2) bond, which is shorter, and the carbonyl bond [C(2)–O(1)] which is longer than the distances found in free peptide units. Apparently the peptide nitrogen is less positive in the chelate than in the free peptide allowing more electrons into the C′–N bond and in

Table 4. *Positional parameters and isotropic temperature factors for hydrogen atoms*

Standard deviation for last digit is in parentheses

	x	y	z	$B(\text{Å}^2)$
H(C1)	0·920 (3)	0·192 (3)	−0·027 (6)	4·1 (11)
H(C3)	0·949 (2)	0·057 (2)	0·413 (5)	2·9 (9)
H(C5)A	0·899 (3)	0·326 (2)	0·122 (5)	3·5 (10)
H(C5)B	0·798 (3)	0·294 (3)	0·151 (6)	5·1 (12)
H(C6)	0·793 (3)	0·316 (3)	−0·151 (6)	5·2 (12)
H(C7)A	0·783 (3)	0·451 (3)	−0·131 (7)	7·1 (15)
H(C7)B	0·840 (3)	0·455 (3)	0·032 (7)	6·7 (15)
H(C7)C	0·735 (3)	0·425 (3)	0·010 (7)	7·6 (15)
H(C8)A	0·915 (4)	0·396 (3)	−0·253 (8)	8·1 (17)
H(C8)B	0·962 (3)	0·393 (3)	−0·086 (6)	5·7 (13)
H(C8)C	0·952 (3)	0·315 (3)	−0·197 (6)	4·8 (11)
H(C9)A	0·900 (3)	0·118 (2)	0·635 (5)	3·1 (9)
H(C9)B	0·950 (3)	0·190 (3)	0·520 (5)	3·9 (10)
H(C11)	0·740 (2)	0·132 (2)	0·672 (5)	3·4 (9)
H(C12)	0·615 (2)	0·212 (2)	0·681 (5)	2·6 (8)
H(C14)	0·746 (3)	0·394 (3)	0·457 (5)	3·9 (10)
H(C15)	0·869 (2)	0·307 (2)	0·433 (5)	2·5 (8)
H(C16)A	0·973 (3)	−0·101 (3)	−0·021 (6)	6·0 (14)
H(C16)B	0·916 (5)	−0·032 (5)	0·087 (9)	11·9 (24)
H(C17)A	1·050 (4)	−0·056 (4)	0·202 (8)	9·8 (20)
H(C17)B	1·083 (4)	−0·022 (4)	0·025 (8)	9·9 (21)
H(C17)C	1·036 (4)	0·043 (4)	0·128 (7)	8·2 (17)
H(N1)A*	0·820	0·123	−0·098	4·0
H(N1)B*	0·759	0·198	−0·036	4·0
H(O4)A	0·634 (4)	0·197 (4)	0·191 (9)	9·7 (20)
H(O4)B	0·661 (3)	0·191 (3)	0·334 (7)	5·4 (12)
H(O5)	0·561 (3)	0·350 (3)	0·647 (7)	7·6 (16)
H(O6)	0·920 (4)	−0·021 (5)	−0·179 (10)	11·9 (23)
H(O7)A	1·085 (5)	0·178 (4)	−0·088 (10)	11·5 (23)
H(O7)B	1·084 (3)	0·232 (3)	0·058 (6)	5·8 (13)
H(O8)A	1·087 (4)	0·104 (4)	−0·336 (8)	9·2 (19)
H(O8)B	1·037 (4)	0·069 (4)	−0·191 (8)	9·1 (18)

* Parameters for these atoms were not allowed to vary during least-squares refinement.

turn more electronic charge to reside on the carbonyl oxygen. In addition it may be noted that the peptide nitrogen has been ionized in the formation of the chelate. This negative charge when delocalized over the system causes a partial negative charge to reside on the oxygen. This provides an alternative explanation for the observed bond distances in the peptide unit. This feature was first observed by Freeman (1967), who gave a different explanation. The short bonds in the ethanol molecule are due to thermal motion which was not corrected for.

Examination of bond angles shows that both N(2) and C(2) of the peptide group are planar with the sum of the angles about the atoms equal to 359·7 and 360·0° respectively. The angles at the copper atom (Table 5) which are included in the chelate rings are decreased significantly from 90°. The value of 108·4° for the O(4)–Cu²⁺–N(2) angle is much larger than the expected value of 90° for a regular square pyramid. It should be noted, however, that the angle subtended by the Cu²⁺–apical oxygen bond and the Cu²⁺–peptide nitrogen bond in square-pyramidal complexes is normally greater than 90° (Blount, Fraser, Freeman, Szymanski & Wang, 1967; Freeman & Szymanski, 1967; Strandberg *et al.*, 1961; Franks & Van der Helm,

1971). This suggests that the effect is possibly due to the presence of the ionized nitrogen of the peptide group.

Table 5. *Bond angles (°) in the copper coordination sphere*

Standard deviation for the last digit is given in parentheses.

N(1)–Cu–N(2)	83·9 (1)°	N(2)–Cu–O(2)′	165·9 (1)
N(1)–Cu–O(3)	163·8 (1)	N(2)–Cu–O(4)	108·4 (1)
N(1)–Cu–O(2)′	101·5 (1)	O(3)–Cu–O(2)′	90·0 (1)
N(1)–Cu–O(4)	99·7 (1)	O(3)–Cu–O(4)	92·9 (1)
N(2)–Cu–O(3)	82·4 (1)	O(2)′–Cu–O(4)	83·7 (1)

A view of the molecular packing is shown in Fig. 5. The peptide chelate forms polymer-like chains about the twofold axis in the c direction with the carboxyl group of the peptide bridging symmetry-related copper atoms. A network of hydrogen bonds involving the waters and ethanol of solvation join the molecules, largely in the a direction. Individual parameters for hydrogen bonds are given in Table 6. The ethanol molecule is seen to lie in channels between the chain of molecules and is involved in only one hydrogen bond. These conditions, along with the fact that the atoms of the ethanol molecule show the highest thermal motion, indicate that the decomposition mentioned previously is probably due to the loss of ethanol from the crystals.

Comparison of the structure of CULT with other copper(II) chelates containing aromatic rings

In the present structure (CULT) we do not find an interaction between the Cu^{2+} ion and the aromatic ring of the tyrosine residue. However, three structures of copper chelates have been reported in which a close contact has been observed between the Cu^{2+} and atoms of the aromatic ring. They are the copper chelates of glycyl-L-leucyl-L-tyrosine (CUGLT) (Franks & Van der Helm, 1971), L-tyrosine (CUTY) (Van der Helm & Tatsch, 1972) and glycyl-L-tryptophane (CUGT) (Hursthouse *et al.*, 1971; Milburn, 1971). Structural parameters related to the interaction are listed in Table 7 for these molecules and CULT. It might be important to note that the interaction in CUGT is not within the same molecule but rather between the Cu^{2+} of one molecule and the aromatic ring of a symmetry-related molecule. The comparison provides some interesting conclusions. It can be seen that the molecules which have an interaction with the copper(II) ion are in the same approximate conformation as is CULT, *i.e.* similar values of the X_1 angle. The conformation of the ring apparently is not the criterion for determining whether an interaction will occur. However the average deviation of the four ligand atoms from the basal plane of the square pyramid seems to be the important consideration. In the molecules in which an interaction is observed the basal plane shows a definite tetrahedral distortion. In CULT the basal plane on the other hand is planar. The planarity of the basal plane in CULT is not caused by the type of chelation. In

fact, the chelation is the same as in the copper(II) chelate of glycylglycine (Strandberg *et al.*, 1961), where for each of the two crystallographically independent molecules the base is planar, but it is also the same chelation found in CUGT where the basal plane is definitely not planar. Although this does little to explain why an interaction does not occur in CULT it presents a possible distinguishing feature, that being the presence or absence of tetrahedral distortion in the basal plane of the copper coordination.

We thank the University of Oklahoma for providing computing facilities.
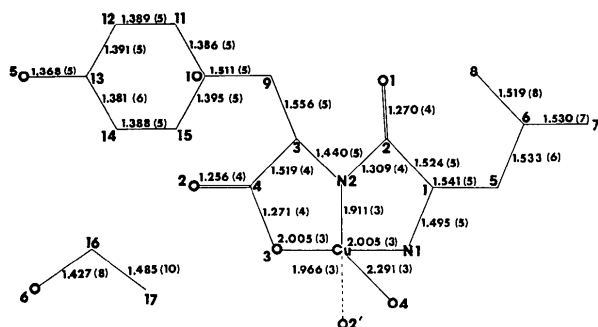
Fig. 3. Bond angles.
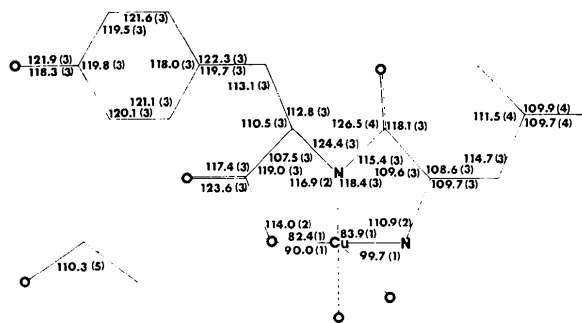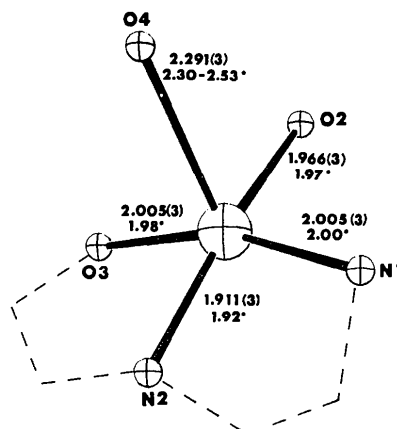

Fig. 2. Bond distances.

Fig. 4. Bond distances involving the Cu^{2+} ion.
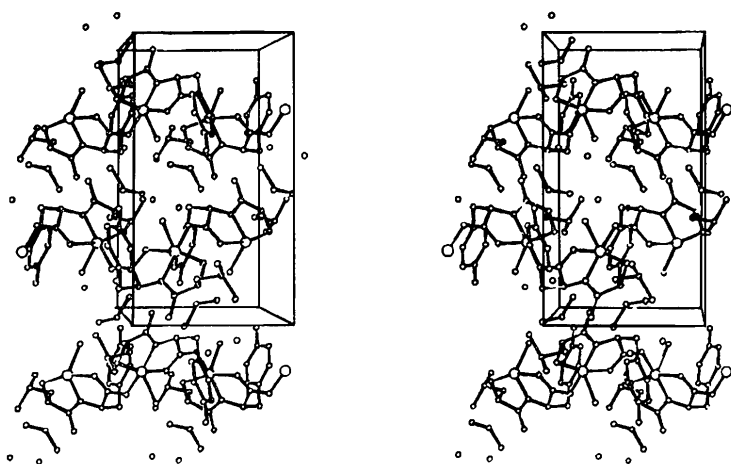

Fig. 5. Stereo view (Johnson, 1965) of the molecular packing.

Table 6. *Hydrogen bonding*

i $-\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$; ii $-\frac{1}{2}+x,\frac{1}{2}-y,1-z$; iii $\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$.

Donor(X)	Acceptor(Y)	Hydrogen(H)	X–H$\cdots Y$	H$\cdots Y$	$X\cdots Y$
O(4)	O(7^i)	H(O4)	170·7°	1·888 Å	2·777 Å
O(5)	O(1^{ii})	H(O5)A	168·2	1·696	2·635
O(7)	O(8)	H(O7)A	154·3	1·736	2·777
O(7)	O(1)	H(O7)B	158·7	2·142	2·955
O(8)	O(5^{iii})	H(O8)A	166·0	2·121	3·019
O(8)	O(6)	H(O8)B	176·8	1·868	2·816

Table 7. *Comparison of the structures of CULT, CUTY, CUGLT and CUGT*

	CULT	CUTY		CUGLT		CUGT
		A	*B*	*A*	*B*	
Cu–C distances	–	–	3·04 Å	3·34 Å	3·21 Å	3·10 Å
less than 3·4 Å			3·11	3·27	3·17	3·20
Average deviation of four atoms from l.s. plane	0·017 Å	0·098 Å		0·155	0·125	0·086
through the basal plane						
X₁ angle	50·7°	295·2°	52·5°	54°	59°	
X₂ angle	80/261	99/278	99/274	90/281	84/274	

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Structure Cristalline et Moléculaire de l'Acide 3R-(1'S-Aminocarboxymethyl) Pyrrolidone-2 5S-Carboxylique C₇H₁₀N₂O₅

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The crystal and molecular structure of 3R-(1'S-aminocarboxymethyl)-2-pyrrolidone-5S-carboxylic acid, C₇H₁₀N₂O₅, has been determined by single-crystal X-ray diffraction. The crystals are orthorhombic P2₁2₁2₁, with unit-cell dimensions $a = 15·301$, $b = 5·326$ and $c = 10·045$ Å; $Z = 4$. The structure was solved by direct methods. The positions of all atoms, including hydrogen, have been refined with anisotropic temperature factors for carbon, oxygen and nitrogen. The final R value is 0·044 for 816 observed reflexions. All bond distances and angles are in good agreement with expected values. Cohesion of the crystal is the result of many short (ionic and van der Waals) interactions.

Introduction

Lors de l'étude des acides aminés libres d'une légumineuse: *Pentaclethra macrophylla*, un nouvel acide aminé a été isolé et identifié par méthodes chimiques et physiques comme étant l'acide 3R-(1'S-aminocarboxyméthyl) pyrrolidone-2 5S-carboxylique (Fig. 1) (Welter, Jadot, Dardenne, Marlier & Casimir, 1975). Sa conformation en solution et sa configuration ab-

solue la plus probable ont été établies par spectrographie r.m.n. et courbes d.r.o. et d.c. Les deux substituants occupent les positions *cis* pseudoéquatoriales sur le cycle lactame prenant une conformation enveloppe analogue à la forme C₅ du cyclopentane. En vue de comparer les conformations de cet acide aminé en solution (Welter & Marlier, 1974) et à l'état cristallin, l'étude par diffraction des rayons *X* de ce composé a été entreprise.