

## The Crystal Structure of Bis-(L-tyrosinato)copper(II)\*

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The crystal structure of bis-(L-tyrosinato)copper(II),  $\text{CuC}_{18}\text{H}_{20}\text{N}_2\text{O}_6$ , has been determined and refined by the least-squares method using three-dimensional X-ray data. The crystals are orthorhombic, space group  $P2_12_12_1$ ,  $Z=4$ , with  $a=13.049$  (7),  $b=22.227$  (8),  $c=6.078$  (3) Å. Diffractometer intensity data were collected for all unique reflections with  $\sin \theta/\lambda$  less than  $0.61 \text{ \AA}^{-1}$ , using Ni-filtered copper radiation. The final  $R=4.2\%$  for all 2012 data. The estimated standard deviations of C, N and O coordinates are between  $0.003$  and  $0.006 \text{ \AA}$ . Coordination of the copper ion is distorted square pyramidal, with ligands in the *trans* configuration. Conformations of the two crystallographically independent tyrosyl residues differ. One of the phenolic rings is located beneath the base of the copper coordination pyramid at a distance slightly greater than  $3 \text{ \AA}$ . This conformation was also observed in the crystal structure of the copper(II) chelate of glycyl-L-leucyl-L-tyrosine. It is interpreted as supporting the hypothesis of a weak interaction between the  $\pi$ -electron system of the phenolic ring and the copper(II) ion.

### Introduction

As part of a study of the interactions between transition metal ions and amino acids and peptides, we have determined the crystal structure of the copper(II) chelate of L-tyrosine (CUTY). Previously it was reported (Van der Helm & Franks, 1968; Franks & Van der Helm, 1971) that a possible weak interaction had been observed between chelated copper(II) ions and the phenolic portion of tyrosyl residues in the structure of the copper(II) chelate of glycyl-L-leucyl-L-tyrosine, CUGLT. This behavior could have had at least two possible causes: (1) a weak interaction between the copper ion and the aromatic  $\pi$ -electron system, or (2) structure-specific effects, such as packing requirements. The implications of a weak interaction, if verified, would prove useful in elucidating the mechanism of certain oxidase enzymes. In order to further examine the possibility of an interaction, we are determining the crystal structures of several related compounds. The copper(II) chelate of L-phenylalanine, CUPA, has been reported (Van der Helm, Lawson & Enwall, 1971) and the structure determination of CUTY is the subject of the present communication.

### Experimental

Single crystals of CUTY were obtained by slow aqueous diffusion of cupric acetate and L-tyrosine at room temperature. Deep blue, thin plates [plate face is (010) plane] appeared at the surface of the tyrosine after 2–3 days. Crystals thus obtained were quite stable; the solution, however, showed slow decomposition after

10–20 days. As the crystals were not appreciably soluble in common solvents, no recrystallization was accomplished.

Crystallographic data (Table 1) and integrated X-ray intensity data were collected, at room temperature, on a G.E.-XRD 5 diffraction unit equipped with a SPG single-crystal orienter, scintillation counter and pulse-height analyzer. The 2012 data, comprising all unique reflections with  $2\theta \leq 140$ , were collected by using Ni-filtered  $\text{Cu } K\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) and  $\theta$ - $2\theta$  scans. This corresponds to a resolution of  $0.82 \text{ \AA}$ . For 193 scans, the intensity was not visibly distinguishable from the background; these were tagged as unobserved and assigned an intensity equal to  $\frac{1}{2}$  of the background at the location of the expected reflection. Lorentz, polarization and absorption corrections ( $\mu=21.4 \text{ cm}^{-1}$ ) were applied to the data. For the absorption correction, the program of Coppens, Leiserowitz & Rabinovich (1965) was used with 216 sampling points. This program uses the numerical integration method of Gauss.

Table 1. *Crystallographic data*

Formula:  $\text{Cu}(\text{C}_9\text{H}_9\text{NO}_3)_2$

F.W. 423.91

Systematic absences:  $h00, h=2n+1$

$0k0, k=2n+1$

$00l, l=2n+1$

Space group  $P2_12_12_1$

$a=13.049 \pm 0.007 \text{ \AA}$

$b=22.227 \pm 0.008$

$c=6.078 \pm 0.003$

(determined by least-squares fit to the  $2\theta$  values of 28 reflections)

$Z=4$

$\rho_c=1.60 \text{ g.cm}^{-3}$

$\rho_o=1.58 \text{ g.cm}^{-3}$

(measured by flotation, at  $24^\circ\text{C}$ , in a  $\text{CCl}_4$ - $\text{CH}_3\text{I}$  mixture)

Crystal dimensions:  $0.6 \times 0.1 \times 0.03 \text{ mm}$

$F(000)=876$ .

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## Structure determination and refinement

A sharpened Patterson synthesis was calculated. The positions of the copper atom were determined from the Harker sections, while 11 nonhydrogen atoms were also located. These atoms were used in a structure factor calculation. The subsequent Fourier synthesis yielded the positions of the remaining nonhydrogen atoms. Block-diagonal least-squares refinement of these atoms using isotropic thermal parameters converged to an  $R = (\sum |kF_o| - |F_c|) / \sum |kF_o|$  of 0.11. All hydrogen atoms, excepting the two hydroxyl hydrogens, were located from a difference Fourier. The hydrogen atom coordinates used in the further refinement were calculated from geometrical considerations and were not refined. They were given isotropic thermal parameters, which were  $\frac{1}{2} \text{ \AA}^2$  larger than those of the atoms to which they are attached. All nonhydrogen atoms were given anisotropic thermal parameters. The observed structure factors were corrected for the anomalous dispersion of copper:  $\Delta f' = -1.862$ ,  $\Delta f'' = 0.604$  (Cromer & Lieberman, 1969). Least-squares refinement of the nonhydrogen atoms, using all the data, was terminated when all parameter shifts were less than 0.1 of the corresponding calculated standard deviations. The final  $R$ , based on the final parameters (Tables 2 and 3), is 0.042 for all data, and 0.034 when the unobserved reflections are excluded. A final difference Fourier showed a number of peaks between  $-0.3$  and  $+0.3 \text{ e. \AA}^{-3}$ .

Table 3. Hydrogen atom parameters

Atomic coordinates are  $\times 10^3$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1) <sub>1</sub>	332	55	-96	2.4
H(1) <sub>2</sub>	433	73	-212	2.4
H(3)	240	90	-332	2.2
H(5) <sub>1</sub>	429	149	-461	2.2
H(5) <sub>2</sub>	309	172	-547	2.2
H(9)	181	210	-268	3.4
H(11)	489	179	-109	3.0
H(13)	163	272	53	3.5
H(15)	469	236	222	3.1
H(2) <sub>1</sub>	389	-145	-443	2.6
H(2) <sub>2</sub>	467	-111	-596	2.6
H(4)	532	-175	-310	2.6
H(6) <sub>1</sub>	680	-110	-263	3.2
H(6) <sub>2</sub>	645	-119	-533	3.2
H(10)	679	-10	-91	3.1
H(12)	561	-35	-730	3.2
H(14)	682	99	-157	3.3
H(16)	560	73	-739	3.3

The atomic scattering factors for  $\text{Cu}^{2+}$ , N, C and O were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for the hydrogen atoms were those of Stewart, Davidson & Simpson (1965). The quantity minimized in the least-squares refinement was  $\sum w(|kF_o| - |F_c|)^2$ , where  $1/w = |kF_o|/P$  for  $|kF_o| \leq P$ , and  $1/w = P/|kF_o|$  for  $|kF_o| > P$ , with  $P = 30$  electrons, giving maximum weight to those reflections which were determined most accurately. A previously described logical routine (Van der Helm &

Table 2. Atomic coordinates ( $\times 10^4$ ) and thermal parameters

The temperature factor is expressed in the form  $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23}) \times 10^{-4}]$ . Standard deviations for the last digit given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>b</i> <sub>23</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>12</sub>
Cu	3886.3 (4)	-326.6 (2)	-3358.6 (9)	38.0 (3)	11.4 (1)	93 (1)	-6.2 (8)	-7 (1)	5.1 (4)
N(1)	3712 (3)	512 (1)	-2265 (5)	41 (3)	10 (1)	69 (8)	-9 (4)	1 (8)	-2 (2)
O(1)	3425 (2)	-5 (1)	-6128 (5)	42 (2)	11 (1)	72 (8)	-6 (4)	-16 (7)	7 (2)
O(3)	2747 (3)	786 (1)	-7754 (5)	48 (2)	14 (1)	104 (8)	10 (4)	-43 (7)	-2 (2)
C(1)	3107 (3)	532 (2)	-6108 (7)	26 (2)	12 (1)	70 (10)	-8 (4)	15 (8)	-9 (2)
C(3)	3116 (3)	870 (2)	-3901 (7)	28 (2)	9 (1)	88 (10)	-9 (5)	2 (9)	-1 (2)
C(5)	3507 (4)	1513 (2)	-4191 (8)	70 (4)	10 (1)	94 (10)	-6 (6)	19 (11)	-4 (3)
C(7)	3392 (4)	1897 (2)	-2130 (7)	45 (3)	8 (1)	153 (14)	8 (6)	35 (10)	-8 (3)
C(9)	2447 (4)	2165 (2)	-1653 (9)	51 (3)	14 (1)	169 (12)	-4 (8)	-36 (14)	-1 (3)
C(11)	4193 (4)	1995 (2)	-724 (8)	39 (3)	14 (1)	134 (12)	7 (6)	13 (10)	-2 (3)
C(13)	2340 (4)	2522 (2)	184 (10)	41 (3)	15 (1)	244 (16)	-22 (7)	26 (13)	3 (3)
C(15)	4104 (4)	2356 (2)	1149 (8)	39 (3)	11 (1)	195 (14)	-1 (6)	22 (11)	-11 (3)
C(17)	3163 (4)	2623 (2)	1570 (9)	50 (3)	9 (1)	145 (12)	4 (7)	4 (13)	-8 (2)
O(5)	3026 (3)	2985 (1)	3425 (6)	58 (2)	13 (1)	186 (10)	-38 (6)	37 (10)	-1 (2)
N(2)	4373 (3)	-1125 (2)	-4531 (6)	40 (2)	12 (1)	84 (9)	-4 (5)	4 (8)	-4 (2)
O(2)	4374 (3)	-0651 (1)	-523 (5)	48 (2)	13 (1)	74 (8)	-10 (4)	1 (7)	16 (2)
O(4)	5308 (3)	-1384 (2)	900 (5)	66 (3)	16 (1)	112 (8)	11 (4)	-1 (8)	18 (2)
C(2)	4941 (4)	-1108 (2)	-702 (7)	44 (3)	12 (1)	97 (12)	12 (6)	2 (10)	-3 (3)
C(4)	5228 (4)	-1306 (2)	-3061 (7)	42 (3)	11 (1)	95 (12)	-1 (6)	-8 (10)	8 (2)
C(6)	6239 (4)	-1002 (2)	-3808 (7)	41 (3)	15 (1)	157 (13)	6 (6)	5 (12)	6 (3)
C(8)	6191 (3)	-316 (2)	-4089 (6)	26 (2)	15 (1)	150 (10)	-1 (7)	26 (10)	4 (3)
C(10)	6546 (4)	71 (2)	-2422 (8)	38 (3)	16 (1)	132 (11)	-10 (6)	6 (11)	-3 (3)
C(12)	5868 (4)	-67 (2)	-6051 (7)	50 (3)	15 (1)	103 (11)	-27 (6)	8 (10)	-1 (3)
C(14)	6571 (4)	694 (2)	-2797 (8)	39 (3)	16 (1)	172 (15)	-24 (7)	-16 (11)	-9 (3)
C(16)	5879 (3)	549 (2)	-6410 (9)	40 (3)	16 (1)	172 (14)	7 (7)	-18 (12)	-12 (3)
C(18)	6263 (4)	927 (2)	-4790 (9)	28 (3)	16 (1)	252 (15)	11 (7)	1 (12)	-2 (3)
O(6)	6306 (3)	1541 (2)	-5222 (7)	50 (3)	15 (1)	422 (15)	21 (6)	-50 (12)	-8 (2)

Table 4. Observed and calculated structure factors

The values of |10kF<sub>o</sub>|, |10F<sub>c</sub>| and calculated phase angles, in centicycles, are given. Unobserved reflections are indicated by a star.

Table with multiple columns (h, k, l, F<sub>o</sub>, F<sub>c</sub>, phase) containing numerical data for various reflections. The table is organized into several sections, likely corresponding to different crystallographic planes or symmetry groups. It includes observed structure factors (F<sub>o</sub>), calculated structure factors (F<sub>c</sub>), and phase angles in centicycles. Some entries are marked with an asterisk to indicate unobserved reflections.

Nicholas, 1970) was also used to optimize the refinement. The list of observed and calculated structure factors is shown in Table 4.

### Description and discussion of the structure

A projection of the structure down the  $c$  axis is shown in Fig. 1. The chelate molecules form infinite chains around screw axes parallel to the  $c$  axis. Perpendicular to these chains the crystal is stabilized by two strong hydrogen bonds (2.62 and 2.71 Å). No other hydrogen bonding occurs in the structure.

The tyrosine residues form two five-membered chelate rings with the copper atom. The residues are *trans* with respect to each other. The copper coordination is square pyramidal. The bond distances and bond angles for the copper coordination are given in Figs. 1, 2 and 3. While the Cu–N distances are similar and compare well with the literature value (2.00 Å),

the Cu–O distances in the basal plane differ considerably (1.925 and 1.973 Å), and the Cu–O(1) distance is significantly shorter than the average value ( $1.98 \pm 0.012$  Å) given by Freeman (1967). The basal plane of the square pyramid is tetrahedrally distorted (Table 5, Fig. 4), while the copper ion is displaced 0.11 Å from this plane toward the top of the pyramid. The two chelate rings are not planar (Planes 2 and 3, Table 5). The nitrogen atoms show the largest deviations (0.22 and 0.65 Å) from the least-squares planes through the carboxylic acid groups. The bond angles in the rings are given in Fig. 3. The nonplanarity of the rings is the result of a rotation around the C<sup>α</sup>–C' bond, by 11.2° for the C(3)–C(1) bond and –29.3° for the C(4)–C(2)

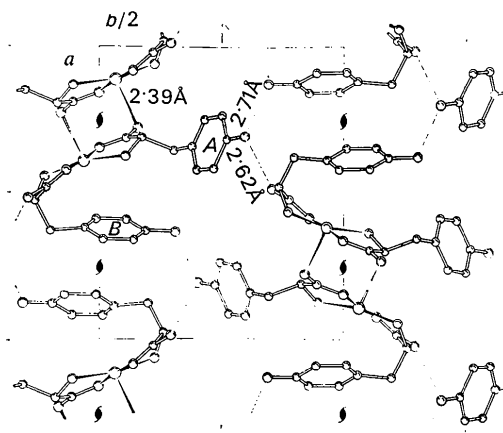


Fig. 1. Projection of the structure down the  $c$  axis.

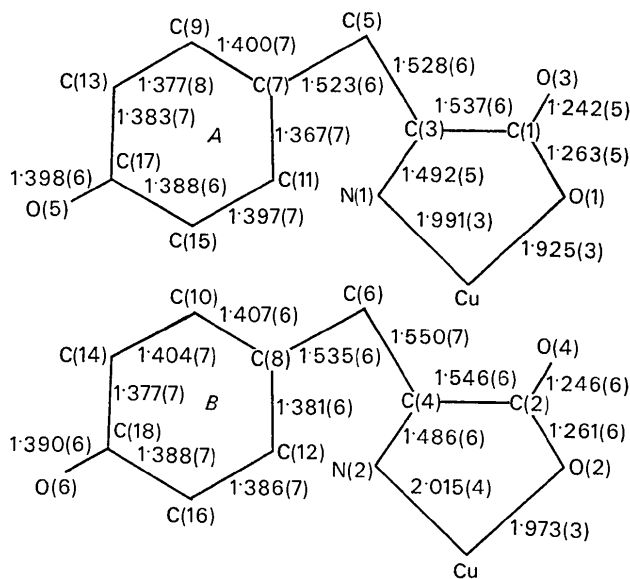


Fig. 2. Intramolecular distances. The estimated standard deviation for the last digit is given in parentheses.

Table 5. Least-squares planes

The equations of the planes are expressed in the form  $Ax + By + Cz = D$ , where  $x$ ,  $y$  and  $z$  are fractional coordinates and  $D$  is the distance from the origin in Å. The method of Schomaker, Waser, Marsh & Bergman (1959) was used to calculate the least-squares planes.

Plane	Atoms		$A$	$B$	$C$	$D$
1	N(1), O(1), N(2), O(2)		12.135	6.686	-1.284	5.039
2	O(1), O(3), C(1), C(3)		11.946	7.563	-1.306	4.894
3	O(2), O(4), C(2), C(4)		10.418	13.383	0.054	3.677
4	C(7), C(9), C(11), C(13), C(15), C(17)		3.470	17.783	-3.268	5.241
5	C(8), C(10), C(12), C(14), C(16), C(18)		12.102	-1.854	-2.215	8.450

	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$
N(1)	0.099 Å	O(1) -0.006 Å	O(2) 0.006 Å	C(5) 0.035 Å	C(6) 0.130 Å
O(1)	-0.098	O(3) -0.006	O(4) 0.006	C(7) 0.005	C(8) 0.007
N(2)	0.098	C(1) 0.017	C(2) -0.016	C(9) -0.002	C(10) -0.005
O(2)	-0.099	C(3) -0.005	C(4) 0.004	C(11) -0.003	C(12) 0.004
Cu	-0.110	N(1) 0.223	N(2) -0.652	C(13) -0.005	C(14) -0.007
O(3')	-2.477	Cu -0.060	Cu -0.084	C(15) -0.003	C(16) -0.017
				C(17) 0.007	C(18) 0.019
				O(5) -0.002	O(6) 0.053
					Cu -2.942

bond. The larger rotation around the C(4)–C(2) bond is reflected in the observation that all bond angles in the chelate ring formed by molecule *B* are smaller than those in the one formed by molecule *A*.

The thermal motion of the atoms in the amino acid residues, observed in the present structure (Figs. 4 and 5), is considerably less than the motion found in the copper chelate of L-phenylalanine. The largest thermal motion is observed for O(6) with 6.57 and 2.66 Å<sup>2</sup> for the temperature factors along the major and minor axes. The bond distances and bond angles in two tyrosine residues are shown in Figs. 2 and 3. The dimensions of the two residues are quite similar. The valence angles of the C<sup>β</sup> atoms are significantly greater (113.4 and 115.6°) than the tetrahedral value. This was also observed for one of the phenylalanine residues in CUPA, and in the structure of the potassium salt of L-tyrosine-*O*-sulfate (Fries & Sundaralingam, 1971). The other distances and angles are normal.

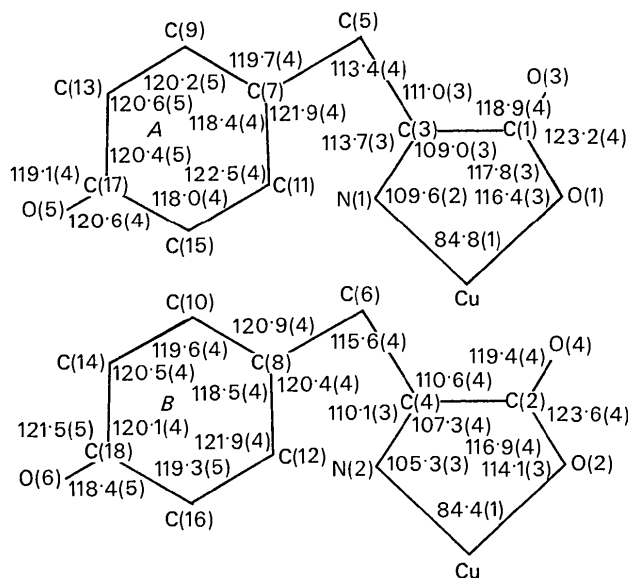


Fig. 3. Bond angles with estimated standard deviations. Other angles at Cu: O(3')–O(1) = 90.8 (1); N(1)–O(2) = 95.0 (1); O(3')–N(1) = 104.3 (1); N(1)–N(2) = 168.0 (1); O(3')–O(2) = 89.8 (1); O(1)–N(2) = 96.7 (1); O(3')–N(2) = 87.6 (1); O(1)–O(2) = 179.3 (1).

The conformation of N and C<sup>γ</sup> about the C<sup>α</sup>–C<sup>β</sup> bond is described by the torsional angle  $X^1$  (Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, 1966). It is found that C<sup>γ</sup> occurs only for values of  $X^1$  close to 60, 180 and 300°, conformations I, II and III respectively (Ramachandran & Sasisekharan, 1968).

For amino acids with aromatic side chains, conformation II seems to be the most common (Pieret, Durant, Griffé, Germain & Debaerdemaeker, 1970). Conformation III has been observed in 3,4-dihydroxy-L-phenylalanine (Becker, Thathachari & Simpson, 1970) and in the two phenylalanine residues in CUPA. Residue *A* in the present structure also has this conformation, with the result that the phenyl group points away from the chelation side. Position I has been observed in L-phenylalanine-HCl (Gurskaya, 1964), in L-tyrosine-*O*-sulfate (Fries & Sundaralingam, 1971) and in CULGLT (Franks & van der Helm, 1971). This conformation is observed for residue *B* in the present structure and allows the phenyl group to be positioned below the base of the square pyramidal copper coordination, as was similarly observed in the CUGLT structure.

The phenyl group of residue *B* is approximately parallel to the basal plane of the metal coordination (Fig. 5, Table 6). There are two close approaches between the Cu<sup>2+</sup> ion and carbon atoms of the phenyl group [C(8): 3.04 Å and C(12): 3.11 Å] (Fig. 4, Table 6). Similar observations were made for both tyrosine residues in the CUGLT structure. The close approaches, as observed, are believed to constitute interactions between the Cu<sup>2+</sup> ion and the phenyl group. It is interesting to note that these interactions do not occur in the CUPA structure. The possible inferences, regarding enzyme mechanisms, of these observations will be published elsewhere.

The basal plane of the square pyramidal copper coordination is tetrahedrally distorted (Fig. 5, Table 5). These distortions (0.10 Å) are similar to those observed in CUGLT, while more than eight times those in the structure of CUPA. It may well be that this distortion is related to the postulated interaction between the Cu<sup>2+</sup> ion and the phenyl group.

Both aromatic rings are planar (Table 5, Planes 4 and 5). The exocyclic atoms C(6) and O(6) in residue *B*, however, show large displacements (0.13 and 0.05

Table 6. Comparison of CUTY and CUGLT

The notations follow the conventions of Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966).

	CUTY		CUGLT	
	Mol. A	Mol. B	Mol. A	Mol. B
Angle between basal plane and phenyl group	—	24°	21°	18°
Cu–C <sup>γ</sup> distance	—	3.04 Å	3.34 Å	3.21 Å
Cu–C <sup>δ</sup> distance	—	3.11	3.27	3.17
Average deviation of the four atoms from basal plane	0.098 Å		0.155 Å	0.125 Å
$X^1$ angle	295.2°	52.5°	54°	59°
$X^2$ angle	99°/278°	99°/274°	90°/281°	84°/274°

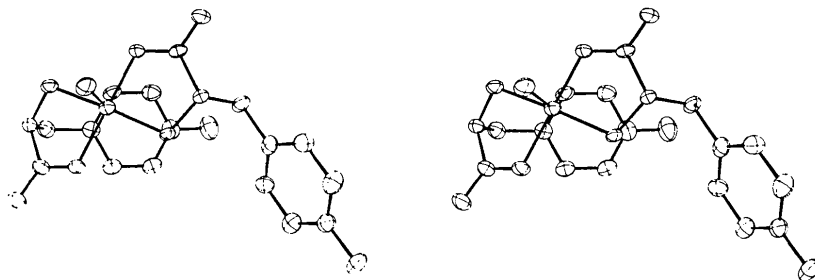


Fig. 4. Stereodiagram (Johnson, 1965) of the structure. The view is along the normal of the phenyl group of residue B.

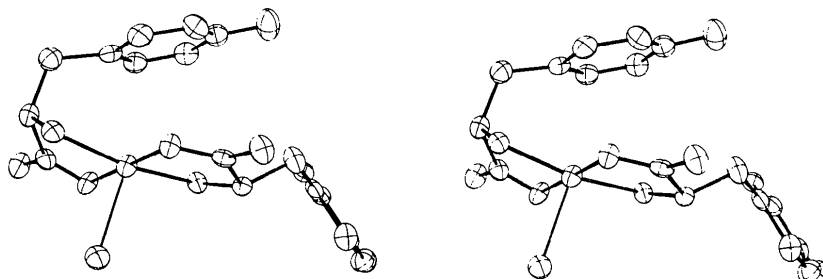


Fig. 5. Stereodiagram. The view is 80° rotated from the one shown in Fig. 4.

Å respectively) from the least-squares plane through the six atoms of the aromatic ring system; the convex side of the aromatic ring is presented to the basal plane of the metal coordination (Plane 5).

All intermolecular distances less than 3.5 Å are listed in Table 7.

Table 7. Intermolecular distances less than 3.5 Å

N(1)	O(1 <sup>i</sup> )	3.086 Å	N(2)	O(3 <sup>i</sup> )	3.063 Å (C)
N(1)	O(3 <sup>i</sup> )	3.468 (C)	O(2)	O(3 <sup>i</sup> )	3.096
N(1)	C(1 <sup>i</sup> )	3.392	O(2)	C(1 <sup>i</sup> )	3.268
N(1)	O(3 <sup>iv</sup> )	3.079	O(2)	C(3 <sup>i</sup> )	3.430
O(1)	O(3 <sup>i</sup> )	3.092 (C)	O(2)	O(1 <sup>iv</sup> )	3.276
C(3)	O(1 <sup>i</sup> )	3.253	O(4)	N(2 <sup>iv</sup> )	3.087
C(15)	O(4 <sup>ii</sup> )	3.415	C(10)	C(12 <sup>v</sup> )	3.477
C(15)	C(5 <sup>iv</sup> )	3.484	Cu	O(1 <sup>i</sup> )	3.388
C(17)	O(4 <sup>ii</sup> )	3.351	Cu	O(3 <sup>i</sup> )	2.391 (C)
O(5)	C(18 <sup>iii</sup> )	3.439	Cu	C(1 <sup>i</sup> )	2.974
O(5)	O(6 <sup>iii</sup> )	2.709 (H)			
O(5)	O(4 <sup>ii</sup> )	2.620 (H)			

The small letter in parentheses indicates that one of the following operations has to be applied to the coordinates given in Table 2:

- |     |                                     |    |                                    |
|-----|-------------------------------------|----|------------------------------------|
| i   | $\frac{1}{2}-x, -y, \frac{1}{2}+z$  | iv | $x, y, 1+z$                        |
| ii  | $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ | v  | $\frac{1}{2}-x, -y, \frac{1}{2}+z$ |
| iii | $-\frac{1}{2}+x, \frac{1}{2}-y, -z$ |    |                                    |

The letter *H* indicates hydrogen bonds, and the letter *C*, distances occurring in the metal coordination.

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