# The Crystal and Molecular Structure of the Dimeric Copper(II) Chelate of Glycyl-L-leucyl-L-tyrosine\*

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The crystal structure of the copper(II) chelate of glycyl-L-leucyl-L-tyrosine, prepared at neutral pH, has been determined and refined by three-dimensional least-squares techniques using 2043 counter data. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a=9\cdot316$ ,  $b=25\cdot76$  and  $c=21\cdot05$  Å. The unit-cell contains four dimeric units of  $Cu_2(glt)_2$ , 32 molecules of water and four molecules of diethyl ether; thus, there are two independent peptide units in the asymmetric unit. The final R value is  $0\cdot103$ . The packing of the peptides is very similar to an anti-parallel pleated sheet structure. It is concluded that the conformation of the peptide is only affected slightly by the chelation. There seems to exist a weak interaction of the copper ions with the  $\pi$ -system of the aromatic rings of the tyrosine groups and the suggestion is made that this interaction correlates with the oxidase activity of certain copper-containing proteins and enzymes.

#### Introduction

The structure of the copper (II) chelate of glycyl-Lleucyl-L-tyrosine (glt) was determined as one in a series of peptide chelate studies to investigate the influence of metal ions on the conformation of peptides and to study the coordination of metal ions in these complexes as well as the hydrogen bonding which occurs. The peptide seemed particularly suitable because both residues contain side chains and one – the tyrosine residue – has an extra functional group. Furthermore the preliminary work indicated the occurrence of two peptides and two copper ions in the asymmetric unit, allowing comparisons of two independent molecules. A note on the unusual coordination geometry observed in this structure has been published (Van der Helm & Franks, 1968).

#### **Experimental results**

The method which was most consistent in yielding crystals of the copper complex of glt proceeded by reacting equimolar quantities of  $CuSO_4$ ,  $Ba(OH)_2$ , both in aqueous solution, and powdered glt. The  $BaSO_4$  was removed by filtration and the resulting chelate solution was approximately 0.055 *M* in peptide. The aqueous solution (*p*H 6–7) was equilibrated with diethyl ether and suitable crystals appeared on standing overnight. The crystals of the complex were well-

formed blue plates which decomposed within one minute on exposure to the atmosphere.

For the X-ray experiments a crystal was transferred in its mother liquor to a thin-walled (0.01 mm) glass capillary. The mother liquor in the capillary was layered with ether. The capillary was then sealed with a small flame during which it was found useful to immerse the capillary in ice water. The systematic absences,  $h00(h \neq 2n)$ ,  $0k0(k \neq 2n)$  and  $00l(l \neq 2n)$ , showed the space group to be  $P2_12_12_1$ . The  $2\theta$ -values of 49 reflections were measured at room temperature (23°C) and used in a least-squares calculation to obtain the cell dimensions which are  $a = 9.316 \pm 0.002$ ,  $b = 25.76 \pm 0.02$  and  $c = 21.05 \pm 0.01$  Å. The density of the crystal could not be measured owing to the instability of the compound. The cell dimensions together with a likely value of the density indicated the contents of the asymmetric unit to be  $Cu_2(glt)_2 \cdot (8-12)H_2O$ . It was not until the structure was fully determined that the actual contents of the asymmetric unit were found to be  $Cu_2(C_{17}H_{23}N_3O_5)_2$ .  $8H_2O$ .  $C_4H_{10}O$ , with a formula weight of 1044.1. The calculated density is 1.37 g.cm<sup>-3</sup> for Z = 4.

The integrated intensities were measured using Nifiltered Cu  $K\alpha$  radiation and the  $\theta$ -2 $\theta$  scan technique on a General Electric XRD-5 diffractometer equipped with a single-crystal orienter and a scintillation counter. The background counts were fairly high and few reflections beyond 2 $\theta$  of 90° had an observable intensity. Of the 2252 independent reflections with a 2 $\theta$  value below 90°, 2044 were observed and used for the subsequent structure determination. Lorentz, polarization and absorption corrections were applied to the data. The linear absorption factor assumed was 1.80 cm<sup>-1</sup>, although on the basis of the composition indicated by the final results of the structure determination a value of 17.0 cm<sup>-1</sup> was calculated. The presence of the

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# Table 1. Parameters of all carbon, nitrogen and oxygen atoms

Calculated standard deviations for the last digit are given in parentheses. Fractional molecule of water, W(1), was located from the last difference Fourier synthesis.

	x	v '	Ζ	В
Molecul	e A	5		_
N(1)	0.525 (2)	-0.0409 (8)	0.0384 (10)	6.0 (5)
C(1)	0.634(2)	-0.0280(8)	0.0847(9)	3.0 (4)
$\overline{C}$	0.566 (2)	0.0133(7)	0.1454(0)	2.2(4)
		-00133(7)	0.1434 (3)	2.2 (4)
O(1)	0.430 (1)	-0.0143(4)	0.1202 (6)	2.5 (3)
N(2)	0.651 (2)	-0.0004 (6)	0.1918 (7)	3.0 (4)
C(3)	0.598 (2)	0.0099 (7)	0.2598 (9)	2.7 (1)
C	0.662(2)	0.00000(7)	0 2376 ())	
0(4)	0.003 (2)	0.0011 (7)	0.2776(9)	2.3 (4)
O(2)	0.791 (2)	0.0714 (6)	0.2632 (7)	4.2 (3)
N(3)	0.583(2)	0.0934(6)	0.3087(7)	3.1 (3)
CÍSÍ	0.648 (2)	0.1422 (0)	0.2214 (10)	4.1 (5)
	0.040 (2)	0.1423(9)	0.3214(10)	4.1 (5)
C(b)	0.282 (3)	0.1627(10)	0.3861 (10)	5.4 (6)
O(3)	0.470 (2)	0.1442 (6)	0.4059 (7)	4.6 (4)
O(4)	0.653 (2)	0.2013(7)	0.4112(9)	7.6 (5)
C		0.2013(7)	04112(9)	1.0 (5)
$\mathcal{C}(\eta)$	0.620 (3)	0.1859 (10)	0.2676 (10)	6.0 (6)
C(8)	0.460 (3)	0.1923 (10)	0.2557 (10)	6.0 (7)
C(9)	0.382(3)	0.1611 (10)	0.2212 (10)	5.2 (6)
CUM	0.220 (2)	0.1(0.0(10))	02212(10)	
	0.229 (3)	0.1009 (10)	0.2125(10)	6·2 (7)
$C(\Pi)$	0.166 (3)	0.2039 (10)	0.2557 (10)	7.0 (7)
C(12)	0.241(3)	0.2371(10)	0.2837 (10)	7.5 (8)
CUN	0.381 (3)	0.2312(10)	0.2040(10)	7 0 (0)
	0.012 (0)	0.2313 (10)	0.2940 (10)	7.0(7)
O(5)	0.013 (2)	0.2047 (8)	0.2499 (10)	8.2 (5)
C(14)	0.649 (2)	-0.0343(8)	0.3033(9)	3.4 (5)
C(15)	0.611 (3)	-0.0900(10)	0.2804(10)	4.9 (5)
CUL	0 449 (4)		0.2004 (10)	4.9 (3)
	0.448 (4)	-0.0944 (10)	0.2847(20)	9.5 (10)
C(17)	0.683 (4)	-0.1284(10)	0.3257 (20)	8.6 (9)
Molecul	e B			(- /
N(1)	0.103(2)	0.1112 (6)	0 2705 (9)	27(4)
	0.193(2)	0.1112(0)	0.3783 (8)	5.7 (4)
	0.080(2)	0.0862 (8)	0.3411(9)	3.1 (4)
C(2)	0.151 (2)	0.0491 (7)	0.2917 (9)	2.9 (4)
O(1)	0.285(1)	0.0420 (5)	0.2950 (6)	3.3 (3)
NO	0.060 (2)	0.0264(6)	0 2533 (7)	
$\Gamma(2)$	0.009 (2)	0.0204 (0)	0.2533(7)	2.9 (4)
C(3)	0.123(2)	-0·0129 (7)	0.2052 (8)	1.7 (4)
C(4)	0.057(2)	0.0029(8)	0.1412(10)	3.1 (5)
O(2)	-0.076 (1)	0.0169 (5)	0.1208 (6)	2.1(2)
N(2)	0 120 (2)		0.1398 (0)	5.1 (5)
IN(3)	0.139 (2)	-0.0019(6)	0.0901 (7)	3.3 (4)
C(S)	0.066 (2)	0.0115 (8)	0.0303 (10)	3.5 (5)
C(6)	0.122(2)	-0.0278(8)	-0.0181(9)	2.8 (4)
0à	0.243 (2)	-0.0506 (6)	0.0082(7)	$\frac{1}{4}$ $\frac{1}{2}$
	0245(2)		-0.0083 (7)	4.1 (3)
O(4)	0.039(1)	-0.0308 (6)	-0.0706 (7)	4.4 (3)
<b>C</b> (7)	0.092 (3)	0.0661 (9)	0.0087 (10)	4.8 (6)
C(8)	0.259(3)	0.0781(10)	-0.0014(10)	4.7 (6)
CÌÓ	0.336 (3)	0.0024 (10)	0.0449 (10)	
C(10)	0 409 (3)	0.0924 (10)	0.0448 (10)	0.2 (0)
C(10)	0.498(3)	0.0998 (10)	0.0369 (10)	6.7 (7)
C(11)	0.549 (3)	0.0854 (10)	-0.0211(10)	6.1 (7)
C(12)	0.467(3)	0.0700 (10)	-0.0642(10)	7.1 (7)
CUI	0.220 (2)	0.0624(10)	0.0002(10)	7 + (7)
	0.320 (3)	0.0634 (10)	-0.0009(10)	/•1 (/)
U(5)	0.697(3)	0.0891 (10)	-0.0256 (10)	11.3 (7)
C(14)	0.060 (3)	-0.0650(10)	0.2309(10)	5.3 (6)
C(15)	0.092(4)	-0.1104(10)	0.1863 (10)	7.8 (8)
CILLÓ	0.021(4)	0.1107(10)	0 1005 (10)	
	-0.031(4)	-0.1197(10)	0.1370(20)	10.0 (10)
$\mathcal{L}(1)$	0.094 (5)	-0.1638 (20)	0.2347 (20)	11.7 (10)
Water n	nolecules			
W(1)	-0.417	-0.150	0.037	10.0
	0.17((2))	0.1075 (10)	0.037	19.0
W(2)	0.170(3)	-0.18/5(10)	0.0034(10)	13.0 (8)
W(3)	-0·140 (4)	-0·2342 (10)	0.0413 (10)	16.2 (10)
W(4)	-0.180(3)	0.1564 (10)	0.0362 (10)	13·0 (8)
Wiss	-0.261 (3)	_0.0382 (10)	-0.0612(10)	12.2 (0)
		-0.0362 (10)	-0.0012 (10)	12.3 (0)
W (6)	0.356 (4)	-0.1265 (10)	0.0918 (20)	17 <b>·9 (10)</b>
W(7)	0.070 (3)	-0·2754 (9)	0.1182 (10)	11.2(7)
W(8)	-0.110 (3)	0.1338 (10)	0.1602 (10)	11.0 (7)
Fther m			0 1002 (10)	$11 \times (1)$
		0.0404 (00)		
$\mathcal{C}(18)$	0.371(6)	-0·2406 (20)	0.3782 (30)	17.4 (20)
C(19)	0.365 (6)	-0.2132(20)	0.4342 (30)	17.9 (20)
O(9)	0.348 (4)	-0·2504 (10)	0.4838 (20)	15.4 (10)
cizón	0.363 (7)	-0.2327 (20)	0.5202 (20)	10.0(20)
C(20)		-0.2327 (20)	0.3393 (30)	19.0 (20)
$\mathcal{O}(21)$	0.387 (1)	-0.2677 (20)	0.2881 (30)	17.7 (20)

capillary and the liquid were neglected in the absorption calculations.

### Structure determination

The positions of the two copper atoms were unambiguously located from a sharpened Patterson synthesis. In order to locate more atoms an eightfold superposition map and a Fourier synthesis phased on the copper atom locations were used simultaneously. It was possible to locate the benzene groups and peptide chains. Three side-chain atoms, *i.e.* two from isopropyl groups and one from a benzene ring, were not found in either map. The peaks of some water molecules were present in both maps. A structure factor calculation was made using the peptide atoms which were located and the two copper atoms. The resulting R index  $(=\sum ||kF_0| - |F_c||/\sum |kF_0|)$  was 0.32.

The trial structure was refined by means of blockdiagonal least-squares computations  $(4 \times 4 \text{ and } 9 \times 9)$ using anisotropic temperature factors for the copper atoms and isotropic ones for the light atoms. When the *R* value was 0.17 a difference Fourier synthesis was calculated. It showed the remaining three sidechain carbon atoms and seven water molecules. These atoms were included in subsequent least-squares cycles. This first difference Fourier synthesis also showed four peaks which were clustered together at distances smaller than hydrogen bond lengths In a second difference synthesis, calculated when the R index was 0.125, a fifth peak appeared in close proximity to the four previously observed. The five peaks formed an extended chain with distances of 1.34, 1.50, 1.38 and 1.34 Å. The peak in the middle had a height of 2.1e.Å<sup>-3</sup> where the other four ranged between 1.26-1.39e.Å<sup>-3</sup>. In addition the peak in the middle was located at a hydrogen bond distance from a water molecule where the distances of the remaining peaks to other atoms in the structure were all larger than 3.5 Å. The group of peaks was therefore identified as diethyl ether, thus explaining the necessity of this solvent for crystallization. All atoms so far located were included in a final series of least-squares calculations. The refinement was terminated when the parameter shifts were smaller than  $\frac{1}{4}$  of the calculated standard deviations. The most pronounced features in the subsequent difference synthesis were two peaks with heights of 1.0 and 0.6 e.Å<sup>-3</sup>, which were close together and at normal hydrogen bond distances from other atoms in the structure. The two peaks had already been observed in the previous difference Fourier synthesis. The peaks were assigned as a disordered molecule of



Fig. 1. Numbering of atoms and notation for conformational angles.

#### Table 2. Parameters for the copper atoms

The anisotropic temperature factors are expressed in the form:

 $\exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)\right].$ 

	x	у	Z	$b_{11}$	b22	b33	b23	b13	<i>b</i> <sub>12</sub>
Cu(1)	0.3268 (3) -	-0·0285 (1)	0.0721 (1)	0.0087 (4)	0.0031 (1)	0.0020 (1)	0.0008 (1)	0.0000 (3)	0.0006 (3)
Cu(2)	0.3935 (3)	0.0911 (1)	0.3504 (1)	0.0094 (3)	0.0021 (1)	0.0021 (1)	0.0010 (1)	0.0002 (3)	0.0003 (3)

water with an occupancy of  $\frac{2}{3}$  and  $\frac{1}{3}$  in the two positions. The position with occupancy of  $\frac{2}{3}$  is listed in Table 1 [W(1)]. The peak with lower electron density was located at x = -0.42, y = -0.135, z = -0.03. The quantity minimized in the least-squares calculations was  $\sum w(|kF_o| - |F_c|)^2$ . The weighting scheme used

throughout the refinement was  $|\sqrt{w} = |kF_o|/P$  if  $|kF_o| \le P$ and  $|\sqrt{w} = P/|kF_o|$  if  $|kF_o| > P(P=41$  electrons). These weights have a maximum for those intensities which are observed most accurately. The intensities of reflections associated with a structure factor larger than 41 electrons required a filter factor bringing them on

## Table 3. Structure factors

The values ( $\times$ 10) for	or $ kF_o $ and	$F_c$ are listed.	All the phase	angles have s	signs opposi	te to tho	se given in this Tabl	le.
E FO PC ALPHA K H= 3, L= 4 0 1 235 284 0.0 2 1 202 250 277-14 3	FD FC ALPHA K 615 681 278.00 900 498 292.63 H= 517 571 305.90 618 630 289.26 0 473 514 51	FD FC ALPHA K - 7 4.L- 7 757 605 0.0 10	FO FC ALPHA R 7 327 341 234.21 O 364 234 144.22 L 9 204 171 314.53 2 7 235 230 172.16 3	F8 FC ALPHA K 519 524 0.0 719 447 240.13 H= 734 739 55.38 843 547 203.97 0	FO FC ALPHA 5, L= 11 139 141 270.00	x FO FC AL 11 578 501 315 12 196 178 191 13 225 216 268 14 148 132 271	РИА К FD FC АЦРИА -10° 11 398 376 274,76 -83 12 298 259 130,71 -92 13 247 232 264,47 -79	
2 420 190 704.48 3 401 401 401 10.48 5 402 401 10.48 4 40 401 10.48 7 404 400 204.57 4 10.40 400 204.57 7 404 400 204.58 10 401 400 204.58 10 400 400 400 400 4000 400000000000000	131         136         24.5         1	200         13         315.12         12           200         13         14         15           100         100         247.16         15           500         207.27         15         16           500         102.27         15         16           517         512.45         16         16           517         512.253.09         17         17           735         757.264.70         14         174.36           337         312.298.40         174.35         175           735         761.140.00         1         134.27         125.40           225         312.140.00         2         125.40         2	000         001         17.42           010         104.154.55         0           040         197.154.51         0           040         197.154.51         0           041         197.154.51         0           041         197.154.51         0           7         141         270         204.19           0         18         223         0.0         10           100         18         74.23         10         10           141         270         204.19         10         10           141         270         20.0         10         10           143         270         20.0         10         10           143         240         74.43         10         10           143         240         74.43         10         10           143         240         74.44         74.43         13	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	224 276 345.07 139 102 240.32 # 325 314 220.279 330 340 66.67 327 371 238.71 305 300 2201.64 225 247 278.66 5, L- 12 226 256 188.66	- 6, L- 6 0 1123 (030 160 1 409 402 43 2 409 741 13 3 544 533 45 3 594 200 125 3 39 341 80 6 215 196 20 7 411 400 125 8 130 124 21 9 451 442 135	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
15 155 153 157.05 17 16 194 154 127.057 17 254 195 114.52 H= 21 384 408 249.04 H= 3, L= 5 2 0 112 90 270.00 3	17 3, L= 12 584 591 180.00 325 366 66.26 446 498 170.61 376 406 346.88 0	237 264 270.43 5 162 117 325.51 6 147 202 0.55 7 4 4, L- 3 9 270 189 90.00 12	100         100 <td>242 272 159.59 3 165 148 70.21 4 5, L= 3 4 447 437 270.00 9 261 275 37.21 10</td> <td>190 263 322.04 312 348 220.00 55 88 267.39 138 186 236.02 × 342 320 196.66 300 281 192.55 99 117 241.89</td> <td>10 312 269 190 12 172 171 103 6, 1= 7 0 652 691 277 1 305 202 234</td> <td>.70 .92 H* 7, L* 5 0 277 254 270.00 1 217 155 104.47 0.00 2 338 243 302.44 .87 3 113 124 457.10</td> <td></td>	242 272 159.59 3 165 148 70.21 4 5, L= 3 4 447 437 270.00 9 261 275 37.21 10	190 263 322.04 312 348 220.00 55 88 267.39 138 186 236.02 × 342 320 196.66 300 281 192.55 99 117 241.89	10 312 269 190 12 172 171 103 6, 1= 7 0 652 691 277 1 305 202 234	.70 .92 H* 7, L* 5 0 277 254 270.00 1 217 155 104.47 0.00 2 338 243 302.44 .87 3 113 124 457.10	
1 1194 1145 177.32 4 2 394 477 87.51 5 3 124 397 87.51 5 4 759 744 71.74 7 5 330 278 102.70 8 4 545 540 81.78 9 7 926 1024 114.91 10 9 726 1024 114.91 10	426 471 49.36 1 298 327 333.21 2 673 656 35.16 3 193 150 317.33 4 400 445 73.41 5 147 144 13.23 6 373 390 138.18 7 144 179 23.41 4	375 425 10-116 14 690 643 79.53 16 592 642 116.44 459 443 87.41 Mm 539 522 145.60 540 538 77.27 0 284 369 227.79 1 197 400 6.44 2	145     65     148.19       6     256     258     189.39       4.     11     7       0     114     72     270.00       1     243     315     8.26       1     271     144.1	448 446 257.76 H+ 555 623 158.15 324 311 800.41 0 883 374 121.42 1 402 584 345.42 3 406 477 40.80 4 145 101 334.42 5	5, L= 13 37 60 270.00 295 417 161.93 217 L63 159.02 309 339 77.17 108 129 328.27	2 427 440 27 4 451 490 102 5 344 354 24 4 132 421 9 7 298 251 28 8 398 358 51 11 182 299 24	-40 - 40 - 412 - 414 - 4	
4 1030 1448 74.277 12 11 070 761 35.21 13 12 340 406 749.06 15 13 424 531 344.40 15 14 334 300 2704.20 15 446 470 354.28 **	153 187 172.29 9 215 199 342.24 10 228 199 342.29 11 306 334 14.83 17 3, L- 13 15	517 510 242.75 3 459 470 346.17 4 182 159 302.43 5 175 101 108.72 4 319 244 52.52 7 206 215 40.70 8 107 115 227.44 10	111 341 411 18460 13 137 186 1847 15 377 279 423 16 381 407 144.41 18 140 188 315.36 193 377 189.44 48 313 293 237.24	526 560 21.26 7 246 175 552.59 10 259 178 154.04 141 221 7.56 He. 190 179 26.98 5, L= 4 2 3	133 206 338.48 146 22 338.34 5, L= 14	13 220 241 25 14 149 197 40 4. L= 8 0 844 870 186 2 974 953 21; 3 511 554 290	7.92 0 223 161 0.0 5.87 1 921 955 265.88 3 314 318 252.88 4 163 178 165.03 7 204 131 66.97 5.00 8 260 229 110.46 1.86 10 312 326 44.77 5.44	
10 140 164 240.55 1 20 215 254 243.15 1 21 151 161 35.07 2 3. L- 6 5 0 547 478 183.00 7	255 269 1.40 19 455 652 195.24 20 377 390 189.57 444 455 182.23 K- 410 400 13.99 152 138 4.62 0 226 258 54.14 1	140         140         202.02         11           183         161         207.08         12           115         139         207.55         14           4, L*         4         H*           824         838         0.0         0           922         912         201.37         1	204 27 207.71 170 170 341.91 4. L= 12 199 207 180.00 240 267 254.88	516 573 0.0 4 505 579 53.64 5 676 684 36.77 7 651 490 24.15 651 704 64.61 Me 283 273 4.60 326 549 306.18 0 183 184 249.67 4	237 188 259.85 271 279 232.11 283 246 257.84 5. L= 15 18 128 90.00 174 241 304.69 1	• 426 573 21 5 547 641 24 6 395 347 21 7 590 550 25 9 219 207 26 12 194 206 25 * 4, L= 9	1.18 H → 7, L → 7 7.00 1.36 L 270 240 330.43 3.40 2 447 421 0.35 1.10 3 L83 L17 3.75 1.73 4 476 407 0.0 4 323 245 333.78 7 53 245 333.88	
L 110 81 700.65 2 921 905 216.38 9 3 172 91 194.00 9 930 957 297.05 11 5 380 349 289.67 5 586 564 108.50 5 385 364 209.22 5 586 568 269.22 5 501 558 269.22 15	403 415 3.16 2 321 309 146.87 3 145 197 350.46 4 504 496 166.81 5 262 227 215.45 6 277 281 166.16 7 378 401 188.31 8 268 259 170.51 10	344         469         36.86         2           584         633         350.92         3         308         349         226.89         6           499         581         47.91         5         765         7793         214.99         6           236         288         75.90         7         320         411         230.15         8           446         435         323.53         9         455.253         9         466         435         323.53         9	2 101 172 100.40 8 5 106 119 128.40 10 41 23 63.73 11 5 370 409 92.88 12 5 318 701 104.56 13 7 323 336 332.55 13 5 05 486 106.87 16 172 287 229.40 16	520 530 274.73 5 288 351 297.45 199 173 5.49 H= 234 181 99.55 244 212 354.24 0 84 117 119.60 2 210 263 343.83 3 128 201 248.00 4	102 104 121.74 6, L+ 0 244 206 180.00 250 192 180.00 386 454 0.0 144 291 0.0	0 414 405 0 1 464 408 16 2 178 129 11 3 546 513 14 4 155 209 27 4 280 332 32 7 396 381 22	8 233 278 514.47 0.00 10 204 246 334.75 7.85 H+ 7, t= 8 1.37 0 459 433 180.00 5.55 1 462 451 261.75 1.49 7 143 151.45	
9 712 669 121.12 10 516 520 231.76 HT 11 602 657 99.46 12 551 554 231.32 0 13 185 175 96.29 1 14 444 651 265.24 3 15 264 259 275.61 6 16 253 274 306.18 5	3, 1-         14         13           257         238         0.0         15           152         175         123.17         17           284         264         202.55         18           472         401         148.80         19           310         366         237.39         10	398 390 345.73 10 344 313 347.84 11 427 414 42.35 12 308 254 174.39 13 282 520 75.15 14 197 157 185.51 183 140 208.35 не	2         279         310         113.03         10           1         398         4.47         248.05         10           2         78         64         28.03         14           5         254         223         249.68         14           116         100         12.76         0           4, 1=         13         1         2	276 293 272.66 4 7 5. L= 5 9 564 606 270.00 11 233 229 73.02 12 594 583 272.78 13 107 272 54.87 14	353 403 0.0 355 422 180.00 114 129 180.00 342 570 180.00 313 392 0.0 753 703 180.00 490 724 0.0 134 135 180.00	8 409 378 32 9 512 495 24 10 292 248 1 11 138 147 23 12 101 200 4	2,44 7 198 354 241.74 4,54 4 113 919 19.92 3,77 4 315 322 37.45 8,77 4 315 322 37.46 4,13 8 29C 222 104.97 7 234 176 91.72 4,13 8 29C 40	
16 221 233 20.11 6 20 211 229 117.44 7 21 166 154 137.06 8 H* 3.L* 7 10 1 1066 1358 171.21 12 2 507 514 168.01 13	566 498 127.81 H* 143 156 250.77 459 492 87.71 0 174 124 85.91 L 524 453 70.60 2 288 329 125.57 3 170 156 85.93 4 206 237 116.44 5	4. L- 5 0 749 678 270.00 2 1219 1343 183.83 3 938 935 346.49 4 568 618 174.63 5 467 618 321.57 6 400 393 94.59 7	0 368 416 90,00 . 1 174 173 241.94 5 2 351 366 73,73 6 3 386 390 240.66 7 5 119 153 78.14 8 5 299 334 303.63 9 181 99 190.44 10 7 159 171 347.12 11	128 201 144.85 15 902 492 55.90 333 335 101.92 H+ 983 581 69.84 185 169 241.01 0 396 450 128.65 11 241 288 204.79 2 425 465 112.56 3	373 386 0.0 6. L= 1 138 256 270.00 341 250 338.45 402 411 215.48 387 383 344.91	0 339 346 1 466 913 29 2 401 412 39 3 671 605 24 4 281 279 30 5 253 267 27 6 228 180 33 7 205 260 31	0.0 5.53 0 147 151 270.00 4.29 2 333 315 222.44 2.84 3 256 212 284.09 2.90 4 106 314 24.41 3.48 7 372 372 94.90 4.61 7 372 372 94.90 4.61 7 7 10	
3 510 543 193.98 14 4 431 497 201.79 6 313 234 19.51 H= 7 170 104 191.57 8 6% 679 79.11 9 164 194 314.28 1 10 242 218 364.46 2 12 47% 537 153.63 3	B2         186         169.31         6           7	222 190 230.24 8 438 409 120.38 10 446 479 191.75 12 294 272 148.03 13 100 123 247.77 326 288 33.03 H= 488 468 31.21 348 320 332.48 0	8 406 239 214.35 13 5 185 197 198.35 14 98 137 190.72 15 5 340 293 240.92 16 4. L= 14 10 5 397 427 180.00	411 395 124.26 4 313 330 73.35 5 150 146 134.19 6 371 404 70.06 7 293 142 97.16 8 5, L= 6 10	455 473 184.51 535 504 184.64 177 230 131.35 542 577 67.31 140 141 227.40 537 647 107.36 301 306 239.09	4 144 248 34 9 141 144 35 10 325 324 32 12 225 220 33 H 4, 1 - 11	4.94 4.24 4.26 4.27 2.148 2.10 1.347 2.15	
13 257 274 554.10 5 14 574 501 104.06 5 15 751 195 94.95 7 16 252 295 109.40 8 17 419 465 351.43 9 18 249 186 356.47 12 19 231 262 17.12 20 339 299 12.66 36	276 218 1.29 16 280 257 256.06 17 419 452 297.05 18 213 252 237.19 20 331 341 288.07 104 136 222.08 He 3. 1- 16 0	250 272 64.14 1 333 284 335.98 2 275 295 146.48 3 -244 252 178.52 5 4, Lu 6 7 302 284 180.00 8	175 172 141.64 0 273 273 166.00 1 5 395 414 175.87 3 5 421 432 191.01 5 220 202 15.56 6 7 326 347 194.15 7 110 106 36.57 6	261 284 0.0 12 471 500 46.79 13 826 876 35.16 14 283 254 40.72 15 620 621 96.18 307 339 50.84 Her 566 624 97.66	230 380 206.57 106 142 193.43 482 481 171.53 194 176 6.77 6, L= 2	1 115 231 3 2 360 332 33 3 251 125 10 4 590 574 33 5 263 329 17 4 268 244 30 7 216 197 18	0.00 H - 7, L 11 0.30 1 188 130 43.27 4.40 0.20 H - 8, L - 0 1.70 4.68 0 202 210 180.30 5.51 1 211 206 3.00	
H= 3, 1= 8 0 0 795 945 0.0 2 2 243 249 300.43 3 3 335 331 278.03 4 4 548 538 278.74 5 5 378 609 140.74 5	214 249 0.0 2 354 416 249.85 3 217 190 80.48 4 228 247 187.48 5 309 279 102.74 6 314 335 137.32 7 244 220 86.48	505 502 315.74 10 529 486 284.48 11 126 229 544.55 16 792 790 326.19 297 370 25.81 H= 619 563 346.08 702 736 14.91 0	211         200         145.78         11           1355         344         132.36         13           4         222         201         12.16         14           4         15         15         16         16           253         247         90.00         He         16	134         174         320.17         1           338         324         17.21         2           259         215         203.00         3           140         148         25.65         4           172         206         145.11         5           5.         L=         7         7	517 570 110.94 306 271 338.08 206 205 72.25 287 249 285.99 244 265 293.01 355 317 80.43 405 388 304.46	H= 6, L= 12 1 220 232 24 2 120 151 13 4 200 211 1 5 245 230 4	2.0 3 2 370 381 10.40 3 373 371 0.0 4 360 330 180.0 2.0 5 147 337 0.0 2.0 6 74 123 180.0 2.0 6 74 123 180.0 2.0 6 74 123 180.0 2.0 9 2.0 9 2.0 9 2.0 10 10 10 10 1.0 10 10 2.0 10 10 1.0	
6 1012 099 212,22 7 7 475 577 340,17 9 8 493 687 264,38 10 9 405 155 140,35 10 456 646 313,18 Hm 11 347 337 31,74 12 356 586 308,96 0 14 293 180 243,18 1	172         125         171.00         0           243         724         240.27         10           226         164         47.56         11           3, L=         17         13           398         409         90.00         14           247         24.146.74         18	293 377 334.13 4 272 297 214.88 5 353 428 318.17 10 319 341 215.01 245 240 245.84 He 126 126 220.65 239 207 27.87 0	292 105 120.11 141 147 191.53 210 219 0.11 4. L= 14 307 259 0.0	193         177         270.00         10           464         453         1.93         11           414         373         180.97         12           405         675         359.78         14           270         322         192.67         15           151         251         2.02         16           382         400         181.28	757 726 69.13 400 408 54.41 201 186 71.98 296 262 325.64 381 329 213.71 499 463 259.06 325 135 165.53	6 376 361 37 8 268 280 28 H= 6, L= 13 0 226 196 27 2 204 206 29 3 182 203 17	3.42         3.75         331         276.00           1         247         256         178.02           2         293         2243         305.16           4         174         174.97         91.35           0.00         7         307.48         324.14           2.03         8         113         144.110.89	
15 227 173 188.50 2 16 341 350 200.16 3 17 252 744 799.57 4 19 143 153 167.03 5 19 114 165 320.56 7 44 3, Le 9 44	47A 484 54.17 147 177 314.68 He 438 408 75.39 314 311 108.02 0 225 273 113.00 1 2 3. L* 18 3	4, L= 7 4 4, L= 7 4 4, L= 7 5 4, L= 7 5	231 249 290.00 11 148 132 201.81 12 246 312 201.81 12 246 310 214.24 14 308 244 339.38 17 313 273 241.21	285         276         218.28           231         225         155.12         0           142         122         19.58         1           140         171         274.40         2           170         121         2.41         3           5r         L*         B         5	271 274 90-00 1 289 247 119.49 400 402 158.75 317 355 88.40 406 60 198.97 442 420 39.74	5 104 152 15 He 7, [= 3 3 274 307 9 4 156 127 27 5 082 667 9 7 474 425 9	a 32 a 3 (c 2 a 134 156 183.00 1 384 370 255.00 0.00 3 405 333 237.35 0.00 4 128 98 24(.13) 0.00 5 158 150 265.23 0.00 5 156 155 165.12	
0 580 626 270.00 0 1 468 432 120.42 2 528 548 322.55 HH 3 963 906 135.54 4 439 461 331.72 0 1 5 658 723 167.38 1 6 336 311 278.71 2 7 499 403 266.11 4	174 224 180.00 5 4. L= 0 7 842 2330 180.00 4 448 470 180.00 10 456 515 180.00 10	42 73 53.73 531 550 289.72 0 634 649 73.52 1 177 179 0.76 2 571 638 106.50 573 591 84.64 Ht 253 214 104.61	5, L+ 0	650 631 183.00 8 419 658 142.14 9 269 282 198.39 10 666 791 153.10 11 236 264 152.17 12 156 232 153.42 13 308 312 128.68 14	346 34 155.03 259 254 265.77 547 516 113.63 303 274 151.22 246 289 111.98 424 416 92.50 118 61 221.04	13 298 336 27 H= 7, L= 1 0 306 269 27 1 250 229 22 2 155 48 29	H+ 4, L+ 3 0.00 0 114 141 40,00 0.50 0 114 141 40,00 0.53 1 186 186 344.76 4.71 2 90 0353-11	
4 214 174 149.41 5 9 417 450 278.20 5 10 185 235 77.33 7 12 494 498 47.08 8 13 334 341 62.04 9 14 279 294 48.44 10 15 255 240 48.77 11 16 170 227 151.75 17	335         426         180.00         13           214         116         180.00         14           280         229         180.00         15           640         689         180.00         16           519         530         140.00         18           757         759         180.00         19           554         490         180.00         19	304 322 285.69 2 380 324 112.10 3 312 317 278.42 4 161 192 128.98 5 238 249 61.30 8 346 355 104.90 9 12	480         720         270.00         10           268         268         270.00         11           141         211.270.00         12           114         63         40.00         13           274         166         40.00         25           216         268         270.00         41	446 451 110.07 171 239 192.92 H= 166 206 113.50 315 428 197.45 0 110 130 198.19 1 5. L= 9 4	517 535 106.22 6, L= 4 173 180 0.0 449 649 105.58 809 710 130.11 243 267 104.06	3 498 435 24 5 340 346 24 4 196 217 16 7 193 170 10 8 517 499 17 9 271 248 6 10 385 309 14 13 237 224 29	1.51         6.16         3.15         1.52         1.61         6           9.63         7         1.91         1.65         80.74           1.56         8.26         H*         3.12         1.67         0.03           5.04         0         1.75         1.67         0.03         1.75         1.67         0.03           5.06         0         1.75         1.67         0.03         1.75         1.67         0.03	
18 191 219 144.72 15 19 213 244 744.72 14 He 3, Le 10 19 0 448 568 180.00 He 1 903 905 281.41	167         125         180.00         N           167         125         180.00         0           154         363         0.0         1           193         139         0.0         2           4, L=         1         4	4, L <sup>4</sup> 8 13 14 331 360 0.0 17 740 718 92.66 18 407 425 64.12 269 288 47.91 H= 331 431 69.31 494 508 312.52 0	5 4-4 474 270.000 7 182 130 40.000 1 7 182 130 40.000 1 7 182 130 40.000 2 5. L= 1 5 7 117 578 90.000 7	5 798 802 90.00 6 298 320 337.96 7 340 430 100.54 8 209 184 187.50 9 177 114 215.19 10 195 224 202.42 11 176 180 245.31 12	619 607 110.84 145 182 151.83 1 468 456 69.58 263 202 270.65 361 402 330.08 351 340 6.29 492 456 274.45 330 288 33.48	H- 7, L= 2 0 537 575 LR 1 L90 258 7 2 411 428 L8 3 L66 154 L1 4 176 119 21	3 107 172 225.60 6 410 346 45.47 6 326 297 24.71 0.00 7.75 H4 4, L+ 5 4.60 4.58 0 115 64 270.00 0.83 1 402 378 4.17	
3 143 104 170 10 1 4 394 324 307,39 2 5 418 324 324 307,39 2 4 207 223 249,40 4 7 786 805 80,30 5 8 9 407 439 24,336 5 9 407 439 24,35 7 10 88 43 44,35 7	Image         View         View         View         View           314         303         243.88         7           834         927         120.84         8           714         841         223.19         9           814         242         114         12           814         242         114.42         11           126         95         216.74         12           451         458         9.24         13           220         169         80.13         14	144 108 41.51 1 690 706 11.81 2 146 156 40.96 7 537 588 25.20 4 351 360 94.07 5 305 329 126.92 6 203 169 39.46 7 260 318 80.59 8	1 1198 1210 173.54 8 9 309 274 314.98 9 679 588 195.10 10 5 95 419 299.45 11 5 936 320 345.51 15 6 437 440 284.77 447 483 55.12 He 363 361 314.95	202 216 173.47 13 214 218 262.30 14 280 270 107.71 15 209 158 250.27 16 313 290 216.16 He he	317 351 263.77 255 235 75.27 243 207 297.70 179 143 139.56 6. L= 5 404 369 90.00	5 97 128 16 6 227 268 35 7 250 256 13 8 116 139 28 10 233 223 18 13 246 226 17 H= 7, L= 3	2.17 2 80 64 187.51 3.29 3 178 152 16.29 4.72 4 91 106 125.93 2.90 5 208 152 84.78 1.55 H= 8.L= 6 0 115 310 0.0	
11 543 533 312.85 9 12 57 46 90.00 10 13 328 247 340.47 11 14 190 142 85.75 12 15 354 370 70.56 13 17 349 354 87.93 14 18 125 186 246.44 15	>>         601         13.47         17           468         548         51.85         140         462         346.15         H=           279         320         271.17         333         281         267.65         0           376         505         271.23         1         280         233         17.54         2           280         232         217.54         2         42         440         62         84         1	285 341 288.50 9 4. L= 9 11 377 422 270.00 14 191 264 48.50 15 651 692 212.36 14 397 410 11 1	440 413 125.33 0 644 603 70.79 1 1 344 365 158.99 2 2 450 431 44.47 4 227 184 19.87 5 373 327 354.70 4 237 398 55 758 7	477 499 180.00 1 217 233 107.36 2 412 471 125.09 3 343 367 125.71 4 257 310 209.46 5 178 203 142.66 4 163 227 208.18 7	610 540 347.18 445 415 44.42 174 192 264.51 213 157 198.20 406 425 215.46 518 518 190.57 181 251 208.75	0 118 120 27 1 165 107 23 2 435 407 18 3 136 177 25 4 327 334 18 5 320 381 24	L 107 148 59.15 0.00 2 276 248 357.72 1.80 4 4 L 3 4.76 44 5 5.74 9 316 278 124.97 5.08 44 10. L 2 5.84 44 10. L 2 5.84 44 10. L 2 5.84 44 10. L 2 5.84 44 10. L 2 5.85 5 5.85	
H= 3, L+ 11 16 20	381 325 260.33 4 246 264 302.84 5 150 140 328.51 6	628 688 196.93 320 291 144.02 H= 320 339 246.11	5, 1= 2 10	303 510 252.47 8 150 180 210.89 9 325 277 287.54 10 196 250 204.74	386 388 299.70 639 632 185.67	415 410 35 10 209 172 52	6.18 7.05 10 750 200 245.84	

Table	3	(cont.)
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K FO	FC ALPHA	K FO FC ALPHA	R PO PC ALPHA	K PO PC ALPHA	& FO FC ALPHA	K FU FC ALPHA	K FO FC ALPHA	K FO FC ALPHA
2 1403 4 1780 6 480 8 543 10 884 12 744 14 924 14 924 14 924 15 926 14 924 14 926 14 926 14 14 926 14 926 14 14 14 14 14 14 14 14 14 14 14 14 14	- 0 3889 0-0 1458 0-0 413 180.00 513 6-0 769 0-0 159 180.00 470 180.00 470 180.00 470 180.00 149 0.0 149 0.0	▶         0, L=         T           1         36         140         270.00           2         212         160         76.00           3         123         110         76.00           4         550         753         76.00           5         166         160.00         71.94           7         1947         1325         270.00           0         1945         1270.00         10           10         164         126.00         11           10         164         126.00         11           10         164         126.00         11           10         164         126.00         11           10         164         100.00         11           10         164         100.00         11           10         164         100.00         11           10         100         100         100         100	1 100 210 270.00 2 1001 1100 0.0 3 101 1100 0.0 5 105 1100 0.0 5 70 257 0.0 1 105 120 257 0.0 1 105 120 20 20 20 20 20 20 20 20 20 20 20 20 2	7 1447 1447 241.18 7 1447 1447 241.18 9 1155 1156 257.24 14 155 1156 257.24 14 155 1156 257.24 15 244 247.55 14 346 444 35.08 14 346 444 35.08 14 316 247.55 15 317 446 77.50 16 157 446 77.50 16 157 446 77.50 16 157 146 77.50 17 146 77.50 17 146 77.50 18 157 146 77.50 19 157 147 147 147 147 147 147 147 147 147 14	1 400 404 177.40 2 356 404 356.01 3 291 275 184.08 4 556 771 319.27 5 340 277 139.27 5 340 277 14 5 340 270 100.44 5 100 270 100.44	5 720 700 0.0 6 153 126 6.0 7 155 149 6.0 8 540 671 6.0 10 1105 1650 6.0 11 149 505 6.0 11 149 505 6.0 13 370 307 160.00 14 370 396 0.0 15 317 376 180.00 15 317 376 180.00 16 153 128 6.0 16 153 128 6.0 17 154 128 6.0 18 153 128 6.0 19 155	Le Leo 151 200-55 Le 230 710 90-56 10 210 710 90-56 10 11 102 100 10,50 27 110 104 25,00 17 110 104 25,00 1 206 1507 90.00 1 206 1507 90.00 1 206 510 90,00 2 405 510 90,00 2 405 510 90,00 5 762 256 75,05 5 111 90 2550-51	3 241 193 14-34 4 401 344 124.03 5 802 312 255.17 7 401 345 30.04 8 331 205 302 455 10 335 30.04 10 335 30.04 10 335 30.04 10 335 30.04 10 347 151.95 12 247 357 155.57 9 7. L 13 0 178 125 270.00
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a common scale with the standard reflection while those with low intensities were affected by adverse counting statistics. The final positional and thermal parameters and their estimated standard deviations, as calculated from the inverse of the least-squares matrix, are given in Tables 1 and 2. No attempt was made to locate the hydrogen atoms in view of the stated purposes of the structure determination, the high temperature factors observed and the large size of the asymmetric unit. The final R value for the 2043 observed amplitudes used in the refinement is 0.103. When the 311 unobserved reflections within the  $2\theta$  limit of 90° are included, the R value is 0.108. A list of the observed and calculated structure factors is given in Table 3. The absorption corrections were calculated on an IBM 1410 computer with a program written by P. J. Schapiro. All other computations were carried out on an IBM 360-40. The structure factorleast squares and Fourier programs used were written by Ahmed (1966a, b). Table 3 was prepared with a program written by Pippy (1967). The atomic scattering factors used for Cu<sup>2+</sup>, O, N and C were those listed in International Tables for X-ray Crystallography (1962).

#### Description and discussion of the structure

## General, chelation sites and metal surrounding

A schematic drawing of a peptide and ether molecule, specifying the atom numbering used, is shown in Fig. 1. Fig. 2 shows a projection of a part of the structure down the b axis.

The atomic positions of Table 1 correspond to the atoms of peptide chains A and B. Some of the carbon atoms in these peptide units are identified in Fig. 2 for clarification. Some of the water molecules are drawn but none of the ether molecules. The reason for the limitations is the length of the projection axis, 25.76 Å. This particular projection, however, shows most clearly the basic building blocks of the structure which are copper-peptide dimers. One dimer is identified in Fig. 2 by labels A and B, for the peptides, Cu(1) and Cu(2). The modes of chelation of the two peptide groups to the metal ions are quite similar. Two five-membered chelate rings are formed by means of the terminal nitrogen atoms of the glycyl residues. N(1), and the carbonyl oxygen atoms of the glycylleucyl peptide groups O(1) of molecules A and B with Cu(1) and Cu(2) respectively. Two other five-membered chelate rings are formed by the deprotonated amide nitrogen atom of the leucyl-tyrosine peptide groups, N(3), and an oxygen atom of the terminal acid groups of A and B with Cu(2) and Cu(1) respectively. Another proof that these particular peptide nitrogen atoms are deprotonated in this complex, formed at pH 6–7, is the trigonal surrounding of both N(3) atoms by Cu, C(4) and C(5). The sum of the bond angles is  $360^{\circ}$  for peptide N(3A) and  $359^{\circ}$  for N(3B) (see Tables 4 and 7). It should be noted that both peptides are doubly deprotonated on the acid end of the molecule.

The five-membered chelate rings form the bases for the square-pyramidal surroundings of Cu(1) and Cu(2). The tops of the pyramids are W(6) for Cu(1) and O(4B) (e) for Cu(2). These fifth bonds are somewhat weaker than those in the basal plane (Van der Helm & Franks, 1968). The atoms forming the bases of the pyramids are tetrahedrally distorted (planes 1 and 2, Table 4), while the copper ions are displaced from the base plane toward the top of the pyramid. Angles and distances in the coordination of the two independent copper ions are given in Table 5. None of the four 5membered chelate rings are planar (planes 3, 4, 5 and 6, Table 4). The rings involving the free acid group are in the half-chair conformation with the peptide nitrogen and copper ion on opposite sides of the leastsquares planes through the acid groups. The chelate

## Table 4. Least-squares planes

The equations of the planes are expressed in the form:

#### Ax + Bv + 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.

1 2 3 4 5	N(1 <i>A</i> ), N(1 <i>B</i> ), C(1 <i>A</i> ), C(5 <i>A</i> ), C(1 <i>B</i> ),	O(1A), O(3B) O(1B), O(3A) C(2A), O(1A) C(6A), O(3A) C(2B), O(1B)		1·481 1·731 0·374 5·017 1·184	23.887 18.412 24.573 17.121 19.556	$ \begin{array}{r} -7.140 \\ 14.193 \\ 6.269 \\ 10.902 \\ -13.438 \\ 9.476 \end{array} $	$ \begin{array}{r} -0.631 \\ 3.789 \\ 1.454 \\ 4.327 \\ -2.798 \\ 0.275 \end{array} $
7	C(3B),	C(0B), C(3B)	(4D)	2.012	19.242	18.105	6.268
8	C(3R)	C(4R), O(2R)	N(3R)	2.768	24.374	2.720	0.500
-	N(1) O(1) O(3) N(3) Cu	$\Delta (1) + 0.16 \text{ Å} - 0.15 - 0.16 + 0.15 - 0.08$	$\Delta (2) -0.13 Å +0.12 +0.13 -0.12 +0.19$	- 100	C(1) C(2) O(1) N(2) N(1) Cu C(3)	$\Delta (3) - 0.00 \text{ Å} - 0.00 \text{ Å} + 0.00 + 0.00 + 0.00 - 0.01 - 0.18 + 0.16$	$\Delta (5) -0.01 Å +0.02 -0.01 -0.01 +0.12 +0.34 -0.07$
	C(5) C(6) O(4) O(3) N(3) Cu		$\begin{array}{c} \varDelta (6) \\ + 0.02 \\ - 0.06 \\ + 0.02 \\ + 0.02 \\ - 0.39 \\ + 0.18 \end{array}$		C(3) C(4) O(2) N(3) N(2) C(5)		$\Delta (8) - 0.01 + 0.02 - 0.01 - 0.01 + 0.93 - 0.04$

rings involving the free amino group are in the envelope conformation.

It was pointed out (Van der Helm & Franks, 1968) that close approaches (between 3.17 and 3.34 Å) (Table 5) occur between the copper atoms and C(8)and C(9) of both tyrosine groups. A similar and even closer approach has now been found in the structure of bis(L-tyrosinato)copper (II) (Tatsch & Van der Helm, 1969). In all three cases the side chains of L-tyrosine fold back so that they are situated below the basal planes of the square pyramidal copper coordination (Fig. 2; Van der Helm & Franks, 1968: Fig. 1). This is a result of the fact that the  $C^{\beta}-C^{\gamma}$  [*i.e.* C(7)-C(8)] bonds are skewed with respect to both N-C<sup> $\alpha$ </sup> [N(3)-C(5)] and C<sup> $\alpha$ </sup>-C' [C(5)-C(6)] bonds. For an L-amino acid that means that the N-C<sup> $\alpha$ </sup>-C<sup> $\beta$ </sup>-C<sup> $\gamma$ </sup> and C<sup> $\prime$ </sup>-C<sup> $\alpha$ </sup>-C<sup> $\beta$ </sup>- $C^{\gamma}$  configurational angles have to be approximately 60° and 300°, respectively. The fact, however, that both these angles are skewed does not necessarily imply that close approaches must occur between the metal atom and the ring in the side chain. For instance in the structure of (β-alanyl-L-histidinato)copper(II) dihydrate (Freeman & Szymanski, 1967), the  $C^{\beta}-C^{\gamma}$  bond of the histidine residue is skewed with respect to the N-C<sup> $\alpha$ </sup> and  $C^{\alpha}-C'$  bonds, but the closest metal imidazole distance is 3.52 Å. It is therefore believed that an interaction exists between the Cu2+ ions and the aromatic rings of the tyrosine groups both in the present structure as in the bis(L-tyrosinato)copper(II) structure. The weakness of the interaction allows for rapid kinetics of reaction. Both the enzymes tyrosinase and laccase, and the protein ceruloplasmin contain copper and have oxygenase activity. It is interesting to note that Levine & Peisach (1962) suggested, on the basis of chemical data, that the enzyme binding in ceruloplasmin to substrate was not through the amine or phenolic group but instead directly to the  $\pi$ -electrons of the aromatic ring. Broman, Malmström, Aasa & Vänngård (1963) hypothesized that the Cu+ ion, which is also present in ceruloplasmin, partakes in substrate binding by interaction with the  $\pi$ -system of the substrate. The present suggestion, however, is the involvement of Cu<sup>2+</sup>, rather than Cu<sup>+</sup>, in this type of binding, or interaction, with the substrate. This interaction, subsequently, allows an electronic reduction-oxidation reaction of the Cu2+ ion with the phenolic group.

## Table 5. Angles and distances in the metal coordination

The literature values are from Freeman (1967). Standard deviations for the last digit are given in parentheses. O(t) is W(6)and O(4B) for the Cu(1) and Cu(2) coordination respectively.

	Cu(1)	Cu(2)	Literature
Cu-N(1)	2·00 (2) Å	2·02 (2) Å	2·00 (1) Å
Cu-O(1)	1.95 (2)	2.00 (2)	1.99 (1)
Cu-N(3)	1.92 (2)	1.98 (2)	1.92 (1)
Cu-O(3)	1.95 (2)	1.94 (2)	1.98 (1)
Cu-O(t)	2.57 (2)	2.32 (2)	
Cu-C(8)	3.21 (3)	3·34 (3)	
Cu = C(9)	3.17 (3)	3.27(3)	

 $c_{\alpha}(1)$ 

Table 5 (cont.)

	Cu(1)	Cu(2)	Literature
O(1)-Cu-N(1)	83 (1)°	82 (1)°	
O(3) - Cu - N(3)	85 (1)	85 (1)	
O(3)-Cu-N(1)	91 (1)	89 (1)	
O(1)-Cu-N(3)	103 (1)	102 (1)	
O(t)-Cu-O(1)	90 (1)	95 (1)	
O(t)-Cu-N(1)	79 (1)	98 (1)	
O(t)-Cu-N(3)	114 (1)	100 (1)	
O(t)-Cu-O(3)	84 (1)	88 (1)	
Cu-N(1)-C(1)	112 (1)°	113 (1)°	111 (1)°
Cu - O(1) - C(2)	115 (1)	116 (1)	113
Cu - O(3) - C(6)	111 (1)	113 (2)	115(1)
Cu-N(3)-C(5)	109 (1)	109 (1)	116 (1)
Cu-N(3)-C(4)	136 (1)	136 (1)	120 (1)
O(1A)-N(3B) O(1B)-N(3A)	3·02 (3) Å 3·09 (3)	O(3B)-N(1A) O(3A)-N(1B)	) 2·81 (3) Å ) 2·78 (3)

Some of the bond angles involving the chelate rings are shown in Table 5 and compared with literature values. The significant differences are in the angles around the N(3) atom. The Cu-N(3)-C(4) angles deviate 16° from the average values (for 5 angles) reported previously (Freeman, 1967). Both in the present structure and in those to which the bond angles are compared, the hydrogen atom on the amide nitrogen atom has been ionized. The important difference between this structure and those with which it is compared. *i.e.* diaquoglycylglycinatocopper(II) hydrate (Freeman, 1967), sodiumglycylglycylglycinato cuprate(II) (Freeman, Schoone, & Sime, 1965) and disodium glycylglycylglycylglycinato cuprate(II) decahydrate (Freeman, & Taylor, 1965), is the fact that more than one chelate ring is formed between the peptide and one particular metal ion in the latter three structures, compared with only one in the present structure. This same feature is the probable cause for the observed differences, from the literature values, of the C'-N-C<sup>z</sup> angles. Freeman (1967) lists an average value of 123° for this angle when the N atom is a part of a chelate ring, which is the same as observed in free peptides (Marsh & Donohue, 1967). In the present structure, however, the C'-N-C<sup> $\alpha$ </sup> angles are 114 and 115° for the peptide nitrogen atoms involved in chelate rings, but 123° (twice) for those which are not a part of a chelate ring (Table 7). It is therefore suggested that when a peptide forms only one chelate ring with a particular metal ion the following angles can be expected around the deprotonated nitrogen atom: Cu-N-Ca, 109°, Cu-N-C', 136° and C'-N-C<sup> $\alpha$ </sup>, 115°, rather than 116, 120 and 123° respectively.

## Bond distances and bond angles

The bond angles and bond distances in the backbone of the peptides, the phenyl and isopropyl groups, and the ether molecule, are shown in Tables 6, 7 and Fig. 3 respectively. In general these values are close to those expected. There are some relatively large deviations in the side groups, but the temperature movement is large for those atoms (Table 1) and the estimated standard deviations are therefore rather large. The bond distances in the backbone of the peptides are similar for the same bonds in the two peptides. The average bond distances compare favorably with those of copper complexes of amino acids and peptides summarized by Freeman (1967). There is one notable exception, namely the bond distances N(2)–C(3) which are 1.54 and 1.52 Å and deviate by  $4\sigma$  and  $3\sigma$  from the literature value of 1.455 (Marsh & Donohue, 1967) for a free peptide or 1.46 Å (Freeman, 1967) for a chelated peptide. The other N–C<sup> $\alpha$ </sup> distances in the present structure are normal.

# Table 6. Bond distances in side-chains and ether molecule

Standard deviations for the last digit are given in parentheses.

$C(5)C(7) \\ C(7)C(8) \\ C(8)C(9) \\ C(9)C(10) \\ C(10)-C(11) \\ C(11)-C(12) \\ C(12) \\ C(12) \\ C(12) \\ C(12) \\ C(13) \\ C(1$	1.62 (3) Å 1.52 (4) 1.30 (4) 1.44 (4) 1.44 (4) 1.25 (4)	1.50 (3) Å 1.60 (4) 1.26 (4) 1.53 (4) 1.36 (4) 1.25 (4)
C(12) = C(13) C(13) = C(8)	1.48 (4)	1.39 (4)
C(11)-O(5) C(3)-C(14)	1.43(4) 1.53(3)	1·39 (4) 1·56 (3)
C(14)–C(15)	1.56 (3)	1.53 (4)
C(15)-C(16) C(15)-C(17)	1·52 (4) 1·53 (4)	1·56 (5) 1·71 (5)
C(18)–C(19) C(19)–O(9)	1·38 (8) 1·42 (7)	
O(9) - C(20) C(20) - C(21)	1·26 (6) 1·40 (8)	

## Table 7. Bond angles

Standard deviations for the last digit are given in parentheses.

Angle	Molecule A	Molecule B
N(1) - C(1) - C(2)	110 (2)°	109 (2)°
C(1) - C(2) - O(1)	120 (2)	118 (2)
C(1) - C(2) - N(2)	117 (2)	117 (2)
O(1) - C(2) - N(2)	123 (2)	125 (2)
C(2) - N(2) - C(3)	123 (2)	123 (2)
N(2) - C(3) - C(4)	105 (2)	106 (1)
N(2) - C(3) - C(14)	109 (2)	103 (1)
C(14)-C(3)-C(4)	112 (2)	112 (2)
C(3) - C(4) - O(2)	121 (2)	119 (2)
C(3) - C(4) - N(3)	117 (2)	117 (2)
O(2) - C(4) - N(3)	122 (2)	124 (2)
C(4) - N(3) - C(5)	115 (2)	114 (2)
N(3) - C(5) - C(6)	107 (2)	105 (2)
N(3) - C(5) - C(7)	115 (2)	114 (2)
C(6) - C(5) - C(7)	108 (2)	112 (2)
C(5) - C(6) - O(3)	119 (2)	119 (2)
C(5) - C(6) - O(4)	115 (2)	118 (2)
O(3) - C(6) - O(4)	126 (2)	121 (2)
C(5) - C(7) - C(8)	110 (2)	112 (2)
C(7) - C(8) - C(9)	125 (2)	120 (2)
C(7) - C(8) - C(13)	118 (2)	117 (2)
C(9) - C(8) - C(13)	116 (3)	122 (3)
C(8) - C(9) - C(10)	124 (2)	121 (2)
C(9) = C(10) - C(11)	113 (2)	114 (2)
C(10)-C(11)-C(12)	121 (3)	122 (3)
C(10) - C(11) - O(5)	111 (2)	113 (2)
C(12) - C(11) - O(5)	126 (3)	125 (3)
C(11)-C(12)-C(13)	123 (3)	127 (3)
C(8) - C(13) - C(12)	118 (3)	114 (3)
C(3) = C(14) = C(15)	115 (2)	112 (2)
C(14) - C(15) - C(16)	106 (2)	112 (3)
C(14) - C(15) - C(17)	108 (2)	105 (2)
C(16) - C(15) - C(17)	111 (2)	106 (3)
C(18) - C(19) - O(9)	107 (4)	
C(19) - O(9) - C(20)	115 (4)	
U(9) - C(20) - C(21)	118 (5)	



Fig. 2. Projection of a part of the structure down the *b* axis. The dashed lines are hydrogen bonds. The numbers indicate carbon atoms.

#### Conformational angles and sheet structure

Least-squares planes were calculated through the four atoms of each of four peptide groups C<sup> $\alpha$ </sup>C'ON (planes 3, 5, 7 and 8, Table 4) and the acid groups (planes 4 and 6, Table 4). These groups are planar. Due to the partial double-bond character of the C'-N bond the C<sup> $\alpha$ +1</sup> atom is supposed to be in the plane of C<sup> $\alpha$ </sup>C'ON. In the present structure the largest deviation occurs for C(3A) (plane 3), 0.16 Å. If least-squares plane 3 is recalculated including the parameters of C(3A), while the largest deviation is for N(2A) 0.06 Å.

An alternative way to describe the peptide backbone is by the use of conformational angles. The conventions and nomenclature adopted for this purpose (Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, 1966) will be used. The angles used are shown in Fig. 1. The calculated values of these angles in the backbone of the peptides for the present structure are given in Table 8. The standard deviation of all conformational angles is estimated to be 2°. The similarity of the  $\varphi$ ,  $\psi$  and  $\omega$  angles for peptides A and B illustrates that both have the same conformation.

#### Table 8. Conformational angles

The  $\psi_3^1$  and  $\psi_3^2$  are the conformational angles involving O(3) and O(4) respectively. The  $\varphi_1$  is the rotational angle of C(1)-C(2) with respect to Cu-N(1). The hydrogen atoms are not located in the structure and  $\omega$  and  $\varphi$  angles are therefore calculated on the assumption that the bonds C'-N, N-H and N-C<sup> $\alpha$ </sup> form a planar set. The columns APPS and PPS give the conformational angles for the antiparallel pleated sheet and parallel pleat structure respectively which were originally proposed by Pauling & Corey (1953). The models proposed by Pauling & Corey were built from D-amino acids. The values given in the Table are for the same models but now built from L-amino acids. The original use of D-amino acids has resulted in confusion in the scientific literature and textbooks (Day & Ritter, 1967). For example the  $\varphi$  angles for pleated sheet structures in Table 3 of Edsall *et al.* (1966) are incorrect.

	A	В	APPS	PPS	
$\varphi_1$	5°	2°			
$\psi_1$	1	7			
$\omega_1$	6	0			
$\varphi_2$	50	49	39°	59°	
$\psi_2$	318	317	318	295	
$\omega_2$	4	1	0	0	
$\varphi_3$	31	38			
$\psi_3^1$	341	337			
$\psi_3^2$	167	168			
	S	ide cha	ins		
				A	В
N(2)-C(3)-	-C(14)-C(1	5) (.	$(X_{2}^{1})$	307°	176°
C(4) - C(3) -	-C(14)-C(1	5)	-	192	62
C(3) - C(14)	-C(15)-C(1	<u>6</u> ) (.	$X_{3^{22}}$	293	268
C(3) - C(14)	-C(15)-C(1	7) (	$X_{3}^{21}$	174	153
N(3)-C(5)-	-C(7) - C(8)	o´ È	$(X_{3}^{1})^{'}$	54	58
C(6) - C(5) -	-C(7) - C(8)	á Š	5,	295	300
C(5) - C(7) -	-C(8) - C(9)	śι	$X_{3}^{22}$	281	274
C(5) - C(7) -	-C(8) - C(1)	<b>3</b> ) (	$X_{3}^{21}$ )	90	84
	-(-) -(-	-, (	<b>.</b> .		

The subscript and superscript notation used for X is that suggested by Ramachandran (1968).

All peptide linkages are *trans*, *i.e.* the C'-O bonds are *trans* to the N-H bonds, which is shown by the values for the  $\omega$  angles: 6, 0, 4 and 1°. The ideal value for a planar *trans* peptide linkage is 0°.

Ramachandran, Ramakrishnan & Sasisekharan (1963) worked out two-dimensional conformational maps correlating the allowed ranges of the dihedral angles around N–C and C –C' in peptides containing residues with a  $\beta$ -carbon atom. New conventions for these angles were established by Edsall et al. (1966), while the subject of conformation of polypeptides and proteins has recently been reviewed (Ramachandran, 1968). This map shows small allowed areas for the right- and left-handed  $\alpha$ -helices, and a much larger area with  $\varphi$  approximately between 20 and 120°, and  $\psi$  between 270 and 360°, in which the peptide chain is stretched, which is the  $\beta$ -structure. The conformational angles of the parallel pleated sheet structure (PPS) and anti-parallel pleated sheet structure (APPS), originally proposed by Pauling & Corey (1953) fall within the area of  $\beta$ -structure on the conformational map.

The  $\varphi_1$  and  $\psi_1$  values involve a glycyl residue and the  $\varphi_3$  and  $\psi_3$  angles the end-acid group. Only the  $\varphi_2$ and  $\psi_2$  angles can therefore be properly compared with standard values.

It was pointed out that in the present structure peptide dimers can be recognized. Peptide A is pointed in the positive c direction while peptide B is pointed in the negative c direction. This general feature is the basic pattern of the antiparallel pleated sheet structure. If this is the basic feature of the structure one would expect the appropriate peptide-peptide hydrogen bonds. These exist in this structure and are shown in Figs.2 and 3: the H-bonds N(2B)-O(2A'') and O(2B)-N(2A'')are formed by the second amino acid residue. The H-bonds of the neighboring residues should then be pointed in the opposite direction and be formed by N(1), O(1), N(3) and O(3) of peptides A and B. These atoms do not form H-bonds but instead form the coordination bonds, in the expected direction, with the copper ions. One generalization of the structure therefore is that it is an APPS structure in which coordination bonds replace hydrogen bonds. The following points conform with this generalization. (a) The  $\psi_2$  angles are very close to those calculated for the APPS model, although the  $\varphi_2$  angles deviate by about  $10^{\circ}$ . (b) The translation distance between chains running in the same direction was proposed to be 9.50 Å by Pauling & Corey (1953); this compares well with the dimension of the *a* axis in this structure of 9.316 Å. (c) Pauling & Corey predicted a repeat distance of 6.68 Å along the chain; that same repeat distance in this structure is the distance between C(1)and C(5), which is 6.64 Å in molecule A and 6.59 Å in molecule B. (d) The  $\varphi_3$  and  $\psi'_3$  angles are comparable with those for an APPS structure as they should be with the third residue having a  $\beta$ -carbon atom and the complex bonds replacing the hydrogen bonds of N(3)



Fig. 3. Bond distances in the backbones of the peptides. The standard deviation for the last digit is given in parentheses.

and O(4). (e) The peptide itself can be crystallized (Hossain & van der Helm, 1969) and the observations obtained so far indicate that it is an APPS structure. On the basis of these observations we suggest that in general the conformational changes in peptides as a result of chelation can be expected to be small when peptide chelates are formed at neutral pH values.

The only large difference between the conformations of the two peptide units is found in the orientations of the isopropyl groups of the leucyl residues: C(14)-C(15) and N(2)-C(3) are *trans* for *B* and skewed for *A*. As noted before the C(7)-C(8) bond has to be skewed both with respect to N(3)-C(5) and C(5)-C(6)for the aromatic ring to be located below the basal plane of the square-pyramidal copper coordination. Table 8 shows that this is the case for both tyrosyl residues.

#### Hydrogen bonding

The hydrogen bonds involved in the formation of the sheet structure have been mentioned. The sheets are linked in the **c** direction by the complex bond O(4B)-Cu(2') and another peptide-peptide hydrogen bond: N(1B) (b)-O(3B) (Fig. 2, Table 9).

Fig. 4 shows a projection of structure down the a axis and is therefore a view approximately parallel to the peptide chains. The cavities between dimers are either filled by ether molecules or water molecules.



Fig. 4. Projection of the structure down the a axis. Atoms N(1) and C(1) for both independent peptides are not shown in this projection. The numbers indicate water molecules. Dashed lines are hydrogen bonds.

The ether molecules are stacked as a column around the  $2_1$  axis parallel to **a**. This column is used to fill the hole that is surrounded by groups of similar polarity, *i.e.* isopropyl groups and phenolic groups. In Fig. 4 this can be seen for instance for the column located at  $\left(-\frac{1}{4},\frac{1}{2}\right)$ . This explains the necessity of ether during the crystallization process. The ether oxygen atom forms an H-bond with W(4). The other cavity in the structure, located at  $\left(\frac{1}{4},\frac{1}{2}\right)$ , is filled by water molecules.

Two hydrogen-bond spirals are present in the structure. One of these is formed by W(7), W(3) and the peptide oxygen atom O(4A) and their symmetry equivalents by a two fold screw axis. The first spiral is connected to a second one formed by W(6), W(1), W(3) and W(2). It is doubtful if W(1)-W(3) is indeed a hydrogen bond. Although the spirals are primarily used to fill the cavity, the hydrogen bond W(2)-O(3A) and the participation of O(4A) and W(6), coordinated to Cu(1), indicates their packing function. The packing is also aided by a hydrogen-bond chain which extends between the ether column and the first hydrogen-bond spiral, *i.e.* O(9), W(4), W(8), O(5A) and W(7). This chain has several branches: W(4)-O(5B), W(8)-O(2B) and W(8)-O(2A). The water molecule that has not been considered yet, W(5), forms two hydrogen bonds: W(5)-O(4B) and W(5)-N(1A). The hydrogen bonds are listed in Table 9, parts A, B and C, and shown in Figs. 2 and 4. The bond not shown in the Figures is W(1)-N(1A), because the angle C(1B)-N(1B)-W(1)makes it doubtful that this is indeed hydrogen bond. The alternative location of W(1), *i.e.*  $W(1^*)$ , with

## Table 9. Intermolecular distances less than 3.50 Å

The atoms in the first column have the coordinates given in Table 1. The small letters following atoms in the second column indicate the operations to be performed on the coordinates of those atoms as given in Table 1.

12

r = 1

4 Pantida nantida H.bo	nde	b c d e f g h	$ \begin{array}{c} x + \frac{1}{2}, \\ -x + \frac{1}{2}, \\ -x + 1\frac{1}{2}, \\ x - \frac{1}{2}, \\ -x + 1, \\ -x - \frac{1}{2}, \\ \end{array} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
A replice-peptice n=00	N(2R) = O(2A)	(a)	2.85 Å			
	O(2B)-N(2A) O(3B)-N(1B)	(a) (b)	2·80 2·91			
B H <sub>2</sub> O-H <sub>2</sub> O H-bonds						
	W(6)-W(2) W(8)-W(4) W(1)-W(3)		2·96 Å 2·75 3·23	W(3)-W(7) W(3)-W(2) W(1)-W(6)	(f) (a)	2·75 Å 2·81 2·55
C H <sub>2</sub> O-peptide and ethe	er H-bonds					
	W(4)-O(5B) W(7)-O(5A) W(8)-O(2B) W(8)-O(5A) W(5)-O(4B) W(5)-N(1A)	(a) (c) (a)	2·45 Å 2·93 3·06 2·86 2·99 2·90	$ \begin{array}{l} W(2)-O(3A) \\ W(3)-O(4A) \\ W(7)-O(4A) \\ W(8)-O(2A) \\ W(1)-N(1A) \\ O(9) -W(4) \end{array} $	(b) (b) (g) (a) (a) (c)	2·70 Å 2·87 2·72 2·85 3·09 2·90
$D W(1^*)$ H-bonds						
	$W(1^*)-W(7)$ $W(1^*)-W(5)$ $W(1^*)-N(1A)$	(f) (a)	2∙96 Å 2∙98 2∙87			
E All other van der Wa	als distances less	than 3.5	0 Å			
	N(1B) - O(4B) W(7) - W(2)	(e)	3·28 Å 3·46	C(17A)-O(5B) W(4) -C(11B) W(4) -C(10B)	(d) (a)	3·48 Å 3·34
	W(7) = C(11A) O(1B) = C(3A) O(1B) = O(4B)	(c) (e)	3·48 3·12 3·19	W(4) = C(10B) O(3A) = O(4B) W(6) = C(15B)	( <i>a</i> ) ( <i>e</i> )	3·33 2·98 3·19
	$C(3B) \rightarrow O(1A)$ C(11B) - N(1A) N(3A) - O(AB)		3·09 3·49 3·29	W(8) -C(10A) W(4) -C(7B) W(5) -O(5B)	(a)	3·45 3·49 3·39
	O(2B) - O(4B) O(2B) - O(1A) O(2B) - O(2A)	(a) (a)	3·16 3·43	W(5) - C(1A) W(5) - N(3A)	(a) (b)	3·23 3·50
	C(1B) - O(2A) C(2B) - O(2A) W(3) - W(2)	(a) $(a)$	3·17 3·45 3·28	$W(1^*) - W(6)$ $W(1^*) - N(1B)$ $W(1^*) - C(1B)$	(a) (h) (h)	3·31 3·25 3·34
	O(2B) - O(2A)	(a)	3.20	$W(1^*) - O(4A)$	(b)	3.26

occupancy of  $\frac{1}{3}$ , has better hydrogen bonds than W(1) itself (Table 9, D). No attempt has been made to indicate donors and acceptors in the hydrogen bonding, because the hydrogen atoms were not located and several bonding schemes are feasible. The large temperature motion of the water molecules (Table 1) is probably the reason that only few reflections with  $2\theta > 90^{\circ}$  could be observed. All other intermolecular distances less than 3.50 Å are shown in Table 9, E.

In summary it is interesting to note that the structure is sufficiently large and complicated for it to be possible to recognize so called hydrophilic and hydrophobic regions.

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## The Crystal and Molecular Structure of 1,8-Dinitrosonaphthalene

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1,8-Dinitrosonaphthalene crystallizes in space group  $P2_1/b$  with  $a=13\cdot13$ ,  $b=16\cdot01$ ,  $c=3\cdot89$  Å,  $=92\cdot7^{\circ}$  and with Z=4. The structure was determined from photographic X-ray data and refined by the least-squares method to R=0.078 for 1009 reflexions. The molecule is in the form of an internal nitroso dimer with an N-N bond  $1\cdot38$  Å long. The naphthalene nucleus shows similar distortions to those found in the acenaphthenes.

#### Introduction

#### Experimental

It is possible to devise a number of plausible molecular structures for 1,8-dinitrosonaphthalene. Data from chemical and spectroscopic measurements do not allow an unambiguous distinction between these structures. Therefore the structure of the crystal was determined by X-ray diffraction. Red-brown crystals of the compound were supplied by Professor M. C. Whiting of Bristol University (Whiting, 1969). The crystal data are:  $C_{10}H_6N_2O_2$ ,  $M=186\cdot 2$ , monoclinic,

 $a = 13 \cdot 13 \pm 0.03, \quad b = 16 \cdot 01 \pm 0.03, \quad c = 3 \cdot 89 \pm 0.01 \text{ Å}, \\ \alpha = 92 \cdot 7 \pm 0.3^{\circ}, \\ Z = 4, \\ D_m = 1 \cdot 51 \text{ g. cm}^{-3} \text{ by flotation}, \\ D_c = 1 \cdot 513 \text{ g. cm}^{-3} \text{ Cu } K\alpha \ 1 \cdot 5418 \text{ Å}, \\ \mu = 9 \cdot 21 \text{ cm}^{-1}.$ 

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