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Crystallographic Studies of Metal–Peptide Complexes. VIII. Glycyl-L-methioninatocopper(II)*

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Abstract. $C_7H_{13}CuSO_3N_2$, $M=268·8$; orthorhombic; $a=10·354$ (6), $b=11·471$ (7), $c=8·872$ (5) Å, $U=1054$ Å^3; $D_x=1·67$ g cm^{-3}, $Z=4$; μ(Mo $K\alpha$)$=22·9$ cm^{-1}; space group $P2_12_12_1$ (No. 19). The copper atom is five-coordinate with square-pyramidal geometry. The equatorial coordination positions are occupied by the amine nitrogen, the peptide nitrogen and a carboxyl oxygen atom of one ligand molecule, and by the free carboxyl oxygen atom of the ligand molecule which chelates a neighbouring copper atom. The apical donor atom is the peptide oxygen atom of the ligand in yet another complex. The side-chain thioether group is not involved in any metal interaction.

Introduction. A water solution of the ligand was allowed to stand in contact with excess solid copper carbonate. Well formed blue crystals of glycyl-L-methioninatocopper(II) were obtained by evaporating the resulting blue solution over silica gel. The dimensions of the crystals used for data collection were $0·18\times0·30\times0·27$ mm and $0·13\times0·24\times0·21$ mm parallel to the *a*, *b* and *c* axes respectively. The intensities were recorded on a computer-controlled Supper equi-inclination diffractometer using the ω-scan technique (Freeman, Guss, Nockolds, Page & Webster, 1970). Two sets of data were recorded, the crystals being mounted about the *b* and *c* axes respectively (Mo $K\alpha$ radiation, graphite crystal monochromator, $2\theta<50°$). The intensity I of a reflexion with an integrated peak count P and background counts of B_1 and B_2 was given by $I=P-(B_1+B_2)$ with variance $\sigma^2(I)=P+B_1+B_2$. Reflexions with $I<2·0\sigma(I)$ were considered to be unobservably weak. The procedures used to correct for Lorentz, polarization and absorption effects, to bring the two data sets to a common scale by a least-squares method, and to calculate standard deviations taking into account both random counting errors and systematic errors, were similar to those described previously (Freeman & Guss, 1972). The final correlated data set had 1416 reflexions (1250 reflexions above the observable threshold). The structure was solved by standard Patterson and Fourier methods, and refined by the full-matrix least-squares method. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2(F)$. In the final cycles all non-hydrogen atoms had anisotropic thermal parameters. Hydrogen-atom positions were found from a difference synthesis and were refined with a damping factor of 0·2. At convergence, the residual $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0·035, and the weighted residual $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·036. The values including unobserved reflexions were 0·045 and 0·040. The final positional and thermal parameters are listed in Table 1.†

Discussion. The structure of one complex is shown in Fig. 1, and the dimensions are listed in Table 2. The Cu atom has a square-pyramidal coordination geometry. It is bonded to one tridentate glycyl-L-methionine ligand at the N(amino) atom N(1), the deprotonated N(peptide) atom N(2), and one of the O(carboxyl) atoms O(2). These donor atoms lie at three corners of the base of the coordination pyramid. The remaining corner of the base is occupied by the free O(carboxyl) atom O(3^{ii}) of the ligand in the symmetrically related complex at $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$, and the apex of the pyramid by the O(peptide) atom O(1^i) of the ligand in the complex at $\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$. The apical Cu–O($1^i$) bond [2·237 (3) Å] appears to be the shortest so far reported in a complex of this type. As a result of the chelation by one ligand and the formation of strong Cu–O bonds to two others, each Cu atom in the crystal lies at the intersection of infinite $-\mathrm{Cu}-\mathrm{O}\overset{\cdots}{-}\overset{|}{\mathrm{C}}\overset{\cdots}{-}\mathrm{O}-\mathrm{Cu}-$ and $-\mathrm{Cu}-\overset{|}{\mathrm{N}}\overset{\cdots}{-}\underset{|}{\mathrm{C}}\overset{\cdots}{-}\mathrm{O}-\mathrm{Cu}-$ chains. The only other inter-complex links are weak hydrogen bonds between N(amino) and chelating O(carboxyl) atoms. The hydrogen bonds occur between the same complexes as are linked by the Cu–O(carboxyl) interactions [N(1)$\cdots$O(2^{ii})$=2·89$ (1), H(N1)$\cdots$O(2^{ii})$=2·21$ (9) Å]. The packing is shown in Fig. 2.

The atoms N(1), N(2), O(2) and O(3^{ii}) lie at 0·055, −0·041, 0·036 and −0·029 Å, respectively, from the

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* Part VII: Freeman, Healy & Scudder (1976).

† A list of structure factors and hydrogen-atom coordinates has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31761 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

plane fitted to them by weighted least squares. The Cu atom is displaced 0·235 Å from this plane in the direction of the apical donor atom O(1^{i}). The peptide group C(1)C(2)O(1)N(2) and the carboxyl group C(3)C(4)O(2)O(3) are planar within the limits of precision. The deviations of the Cu and C(3) atoms from the peptide group plane (−0·363 and −0·187 Å), and the deviation of the Cu atom from the carboxyl group

Table 1. *Final fractional positional coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^3) *for glycyl*-L-*methioninatocopper*(II)

The scattering factor for an atom is expressed as:

$$f_0 \exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	2275·1 (5)	1124·4 (4)	211·2 (6)	16·6 (2)	23·0 (3)	17·4 (2)	4·9 (2)	1·0 (2)	−0·6 (2)
S	1658 (2)	4203 (1)	−4926 (2)	69 (1)	37·8 (7)	42·1 (9)	−7·1 (6)	−11·6 (8)	13·0 (7)
O(1)	−1328 (3)	2388 (3)	−251 (4)	22 (1)	35 (2)	43 (2)	8 (1)	1 (2)	−7 (2)
O(2)	2468 (3)	350 (3)	−1821 (4)	28 (2)	39 (2)	28 (2)	15 (2)	−6 (1)	−13 (1)
O(3)	1403 (3)	−29 (3)	−3984 (4)	32 (2)	38 (2)	24 (2)	12 (1)	−6 (1)	−12 (1)
N(1)	1517 (4)	1855 (4)	2144 (5)	31 (2)	28 (2)	24 (2)	6 (2)	1 (2)	−1 (2)
N(2)	741 (3)	1734 (3)	−714 (4)	17 (2)	24 (2)	20 (2)	3 (1)	−2 (1)	−3 (1)
C(1)	206 (5)	2312 (5)	1838 (6)	23 (2)	40 (3)	26 (3)	5 (2)	5 (2)	−4 (2)
C(2)	−191 (4)	2156 (3)	150 (5)	21 (2)	19 (2)	28 (2)	1 (2)	2 (2)	−2 (2)
C(3)	468 (4)	1377 (4)	−2282 (5)	20 (2)	25 (3)	24 (2)	6 (2)	−2 (2)	−5 (2)
C(4)	1525 (4)	495 (4)	−2722 (5)	23 (2)	24 (2)	23 (2)	0 (2)	1 (2)	−2 (2)
C(5)	448 (5)	2407 (5)	−3431 (6)	32 (3)	34 (3)	27 (3)	8 (2)	−7 (2)	3 (2)
C(6)	1753 (6)	3023 (5)	−3553 (7)	44 (3)	39 (3)	35 (3)	−1 (3)	−7 (3)	9 (2)
C(7)	3099 (7)	5006 (5)	−4466 (8)	59 (4)	37 (3)	60 (4)	2 (3)	3 (3)	5 (3)

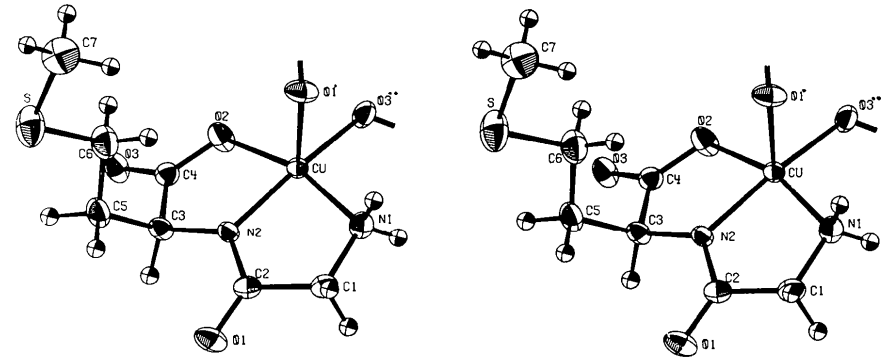

Fig. 1. Stereoscopic view of glycyl-L-methioninatocopper(II) showing vibrational ellipsoids (50 % probability level).

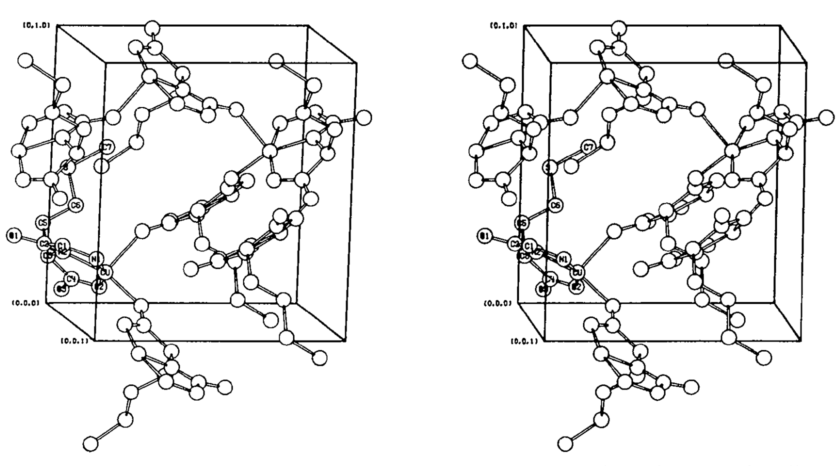

Fig. 2. Packing of glycyl-L-methioninatocopper(II) complexes in the unit cell.

Table 2. *Bond lengths* (Å) *and angles* (°)

Symmetry code
Superscript
(i) $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$
(ii) $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$

Cu—O(1^{i})	2·237 (3)	O(3)–C(4)	1·278 (6)
Cu—O(2)	2·020 (3)	N(1)–C(1)	1·480 (7)
Cu—O(3^{ii})	1·990 (3)	N(2)–C(2)	1·323 (6)
Cu—N(1)	2·064 (4)	N(2)–C(3)	1·477 (6)
Cu—N(2)	1·920 (4)	C(1)–C(2)	1·564 (7)
S—C(6)	1·823 (6)	C(3)–C(4)	1·540 (6)
S—C(7)	1·800 (7)	C(3)–C(5)	1·561 (7)
O(1)–C(2)	1·257 (5)	C(5)–C(6)	1·528 (8)
O(2)–C(4)	1·273 (6)		

O(1^{i})–Cu—O(2)	106·6 (1)	Cu—N(2)–C(2)	119·2 (3)
O(1^{i})–Cu—O(3^{ii})	91·8 (1)	Cu—N(2)–C(3)	117·3 (2)
O(1^{i})–Cu—N(1)	85·6 (2)	C(2)–N(2)–C(3)	120·5 (4)
O(1^{i})–Cu—N(2)	105·3 (1)	N(1)–C(1)–C(2)	112·1 (4)
O(2)—Cu—O(3^{ii})	88·5 (1)	O(1)–C(2)–N(2)	126·6 (5)
O(2)—Cu—N(1)	163·3 (2)	O(1)–C(2)–C(1)	119·5 (4)
O(2)—Cu—N(2)	82·0 (1)	N(2)–C(2)–C(1)	113·9 (4)
O(3^{ii})–Cu—N(1)	102·7 (1)	N(2)–C(3)–C(4)	106·6 (4)
O(3^{ii})–Cu—N(2)	162·2 (2)	N(2)–C(3)–C(5)	114·0 (4)
N(1)—Cu—N(2)	83·8 (2)	C(4)–C(3)–C(5)	109·9 (4)
C(6)—S—C(7)	100·6 (3)	O(2)–C(4)–O(3)	124·4 (4)
Cu—O(1^{i})–C(2^{i})	139·6 (3)	O(2)–C(4)–C(3)	118·1 (4)
Cu—O(2)—C(4)	115·3 (3)	O(3)–C(4)–C(3)	117·5 (5)
Cu—O(3^{ii})–C(4^{ii})	122·9 (3)	C(3)–C(5)–C(6)	112·6 (4)
Cu—N(1)—C(1)	109·9 (3)	S—C(6)–C(5)	110·1 (4)

plane (−0·270 Å), are significant. In view of the current interest in the extent to which peptide groups remain planar under various conditions it is important to note that the atoms Cu and C(3) not only deviate from the peptide group plane but lie on the same side of it. It follows that the three bonds formed by the N(peptide) atom N(2) are not coplanar, which is also shown by the sum of the bond angles at N(2), 357° (Table 2).

The deviations of individual atoms from the planes specified in the preceding paragraph are expressions of the conformation of the chelated portion of the complex (the 'puckering' of the chelate rings). A convenient way to describe the conformation of a chelate complex is to specify the dihedral angles between adjacent three-atom segments having the metal atom in common (Freeman, Healy & Scudder, 1976). For the sake of future comparisons we here record the dihedral angles between planes fitted, respectively, to CuO(2)C(4), CuC(4)C(3), CuC(3)N(2), CuN(2)C(2), CuC(2)C(1) and CuC(1)N(1): 8·4, −3·7, −19·2, 10·2 and 2·3°. The shortest non-bonded contact of the side-chain C_β atom is with the non-chelating O(carboxyl) atom of the methioninato residue [C(5)···O(3) = 3·00 Å]. It is this contact rather than the contact with the O(peptide) on the other side [C(5)···O(1) = 3·37 Å] which determines the equilibrium combination of side-chain orientation and chelate conformation.

Our original reason for studying this complex was to obtain information about the behaviour of the methionine thioether group. The $-CH_2-CH_2-S-CH_3$ side chain is in an extended conformation. The torsion angles $\chi^{1,1}$, $\chi^{1,2}$, χ^2 and χ^3 about the central bonds in the sequences N(2)–C(3)–C(5)–C(6), C(4)–C(3)–C(5)–C(6), C(3)–C(5)–C(6)–S and C(5)–C(6)–S–C(7) are 62·7 (6), −56·9 (6), 179·4 (4) and 164·5 (5)° respectively. The absence of any interaction between the Cu atom and the thioether side chain is consistent with earlier observations on bis-(D,L-methioninato)copper-(II) (Veidis & Palenik, 1969), and is in marked contrast with the metal binding in chloro(glycyl-L-methioninato)platinum(II) hydrate, *cis*-dichloro-(L-methionine)-platinum(II) and *cis*-dichloro-(D,L-methionine)platinum(II) (Freeman & Golomb, 1970). In the platinum complexes there are strong metal–sulphur bonds, resulting in the formation of six-membered chelate rings, while the carboxyl groups are neutral (protonated) and free.

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