

## The Structure of a Copper Complex of an Essential Sulphur-containing Amino-acid; bis(Methioninato)copper(II)

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*Summary* The first crystal structure of a copper complex of a sulphur-containing amino-acid, bis(methioninato)-copper(II), has shown that the sulphur atom is not coordinated to the metal ion, suggesting a possible model for *trans*-methylation reactions.

THE crystal structure of bis(methioninato)copper(II) is the first structural study of a copper complex of a sulphur-containing amino-acid and of a first-row transition-metal complex of methionine. The metal chelates of this essential amino-acid show some antibacterial activity<sup>1</sup> and may be

involved in the synthesis of cysteine.<sup>2</sup> Since methionine has three groups, C-S-C, NH<sub>2</sub>, and CO<sub>2</sub>H capable of co-ordinating to a given metal ion, a knowledge of the structures of the metal chelates is essential for understanding the behaviour of methionine.

Blue crystals, from water, were studied by X-ray diffraction, using Cu-K<sub>α</sub> radiation: Cu(C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>S)<sub>2</sub>, *M* = 395.95; monoclinic, space group *P*2<sub>1</sub>/*a* (No. 14), *a* = 9.482(5), *b* = 5.018(4), *c* = 16.035(13) Å, β = 93.78(4)°, *D*<sub>m</sub> = 1.596 g/cm<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.569 g/cm<sup>3</sup>. The structure was solved by the heavy atom method using 1096 non-zero

reflections with  $2\theta \leq 135^\circ$  measured with a G. E. diffractometer. The structure was refined by full-matrix least-squares methods using anisotropic thermal parameters to a

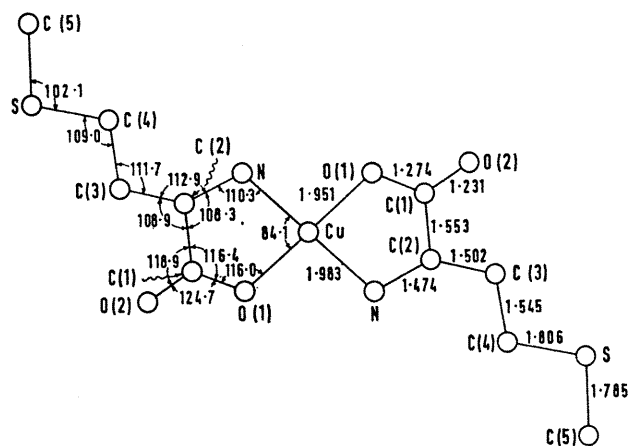


FIGURE. The atomic numbering, bond distances, and angles in bis(methioninato)copper(II). A centre of symmetry at the copper atom relates one methionine group to the other.

<sup>1</sup> W. O. Foye, *Fed. Proc.*, 1961, **20**, Suppl. No. 10, 147.

<sup>2</sup> S. K. Shapiro and F. Schlenk, "Transmethylation and Methionine Biosynthesis," University of Chicago Press, Chicago, Illinois, 1965.

<sup>3</sup> C. A. McAuliffe, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, 1966, **5**, 1996; and S. E. Livingston and J. D. Nolan, *ibid.*, 1968, **7**, 1447.

<sup>4</sup> N. C. Stephenson, J. F. McConnell, and R. Warren, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 553.

<sup>5</sup> A. McL. Mathieson, *Acta Cryst.*, 1952, **5**, 332.

final  $R$  of 0.073. Seven of the ten hydrogen atoms (the three hydrogens on the terminal methyl group were not locatable) were included in the calculations, but were not refined.

The atomic numbering, bond distances, and angles are illustrated in the Figure. The co-ordination about the copper atom is that of a distorted octahedron. The methionine co-ordinates through one oxygen, O(1), of the carboxy-group and the nitrogen, N, from the amino-group. The copper atom is at a centre of symmetry so that the Cu, O(1), and N form a square-planar arrangement. The octahedron is completed by a long Cu-O(2) bond of 2.713 Å.

The sulphur atom does not co-ordinate with the copper atom, in agreement with previous conclusions based on spectral studies of the metal complexes.<sup>3</sup> Although in the palladium chloride-methionine complex the sulphur atom is bonded to the palladium atom,<sup>4</sup> the side-chain is fully extended in the copper complex with C(5) *trans* to C(3), similar to the configuration found in  $\beta$ -methionine.<sup>5</sup> The absence of an interaction between the sulphur and the copper atom leaves the -SCH<sub>3</sub> group available for further reaction. Therefore, *trans*-methylation reactions involving methionine could utilize a copper chelate as an intermediate.

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