The Crystal and Molecular Structure of Copper(II) Bis-2,5-dimethyloxazolidine-4-carboxylate Dihydrate. Relation between the Structure of the Complex and the Synthesis of DL-Threonine

By J. P. AUNE and P. MALDONADO

(*Institut de Pétróléochimie, Faculté des Sciences*, 13, *Marseille* 13e, *France*)

G. LARCHERES

(*Laboratoire de Chimie-Physique, Centre Universitaire de Marseille-Luminy*, 13, *Marseille* 8e, *France*)

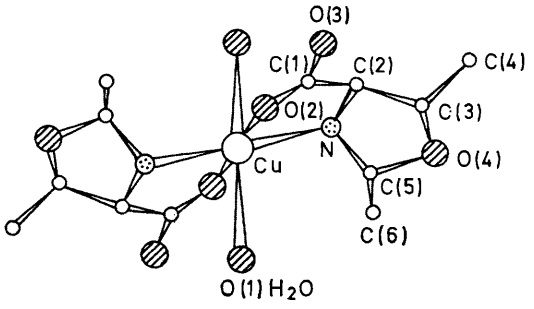
and M. PIERROT*

(*Laboratoire des Mécanismes de la Croissance Cristalline, associé au C.N.R.S. Faculté des Sciences*, 13, *Marseille* 13e, *France*)

Summary The structure of the copper(II) complex $C_{12}H_{24}O_8N_2Cu$ formed during the synthesis of the DL-threonine is that of an oxazolidine, a fact which enables a reaction mechanism to be established for this synthesis of threonine.

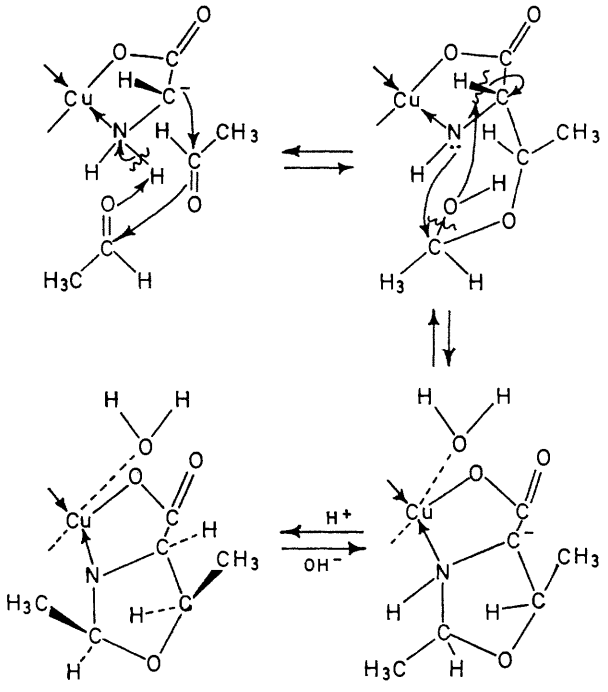
CONDENSATION of glycine with an excess of acetaldehyde was performed, in basic aqueous solution, in the presence of a stoicheiometric amount of copper(II) basic carbonate, and an intermediary complex of molecular formula $C_{12}H_{24}O_8N_2Cu$ was isolated. The decomplexation of this compound in an acid medium by H_2S releases threonine in the aqueous solution, the copper being recovered in the form of insoluble CuS. The interesting point of this synthesis is to orientate the reaction towards the formation of a preponderant quantity of the DL-threonine isomer.

The structure found for the intermediary complex



FIGURE

Bonds	Lengths (Å)	Bonds	Angles (degrees)	Bonds	Angles (degrees)
Cu–O(1)	2·542	O(1)CuO(2)	95·46	O(4)C(3)C(4)	112·61
Cu–O(2)	1·962	O(1)CuN	98·75	C(2)C(3(C(4)	111·95
Cu–N	2·013	O(2)CuN	83·86	O(4)C(5)N	103·85
O(2)–C(1)	1·278	O(3)C(1)O(2)	127·40	O(4)C(5)C(6)	108·51
C(1)–O(3)	1·216	O(2)C(1)C(2)	115·33	NC(5)C(6)	115·39
C(1)–C(2)	1·569	O(3)C(1)C(2)	117·27	CuNC(2)	108·31
C(2)–N	1·501	C(1)C(2)N	110·61	C(2)NC(5)	106·09
C(2)–C(3)	1·595	C(1)C(2)C(3)	108·93	C(5)NCu	116·38
C(3)–O(4)	1·463	NC(2)C(3)	103·59	C(3)O(4)C(5)	106·54
C(3)–C(4)	1·569	O(4)C(3)C(2)	102·53	CuO(2)C(1)	115·95
O(4)–C(5)	1·415				
C(5)–N	1·506				
C(5)–C(6)	1·483				



$C_{12}H_{24}O_8N_2Cu$ made it possible to explain the preferential orientation of the reaction towards the DL-*threo*-form. In addition, this result invalidates the formulae suggested earlier[1,2] and a crystallographic study[3] which seems incomplete and incorrect.

The complex $C_{12}H_{24}O_8N_2Cu$ crystallised in the monoclinic space-group $P2_1/c$ with: $a = 11{\cdot}32(2)$; $b = 7{\cdot}17(2)$; $c = 10{\cdot}62(2)$ Å; $\beta = 100° + 1°$. $D_m = 1{\cdot}49 \pm 0{\cdot}03$; $D_c = 1{\cdot}51$ with $Z = 2$ and $M = 387{\cdot}57$.

The intensities of 600 reflexions were measured by means of a Weissenberg camera. The structure was resolved by the usual methods (Patterson function, Fourier series, and least-squares procedure). The final R-factor is 0·116.

The standard deviations for the bond lengths vary from 0·02 to 0·04 Å and for the angles from 1 to 2°.

The molecular structure is shown in the Figure. It comprises four five-membered rings, two resulting from the complexation of the amino-acid on the copper atom, and the other two having substituted oxazolidine structures. The hexagonal co-ordination of copper is completed by two water molecules and the amino- and carboxylic groups.

These results agree with those of absorption spectra carried out in the i.r. and in the visible region; they indicate the following reaction mechanism for the formation of the complex: the base OH^- removes one of the two active hydrogens of copper glycinate. The anion formed attacks an acetaldehyde molecule. The alkoxide anion thus formed attacks a second acetaldehyde molecule with the formation of a hemiacetal which cyclises on to the neighbouring nitrogen atom to give an oxazolidine with the expulsion of one water molecule. The acidification of the medium leads on the whole to the DL-*threo*-complex, which is thermodynamically the most stable. This complex is insoluble in aqueous medium and is recovered by filtration. The decomposition of the complex in acid medium by H_2S releases the DL-threonine and the acetaldehyde which served to form the oxazolidine ring, whereas the copper is precipitated in the form of insoluble CuS.

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[3] S. Imado, *J. Pharm. Soc. Japan*, 1961, **81**, 832.