

Tableau 4. Environnement du cuivre dans différents carboxylates de cuivre monopyridiné

	Cu-Cu	Cu-N	Cu-O	
Cu(CH ₃ CH ₂ COO) ₂ .C ₅ H ₅ N (i)	2,642 (2) Å	2,17 (1) Å	1,96 (1) Å	1,95 (1) Å
	2,619 (2)	2,13 (1)	1,96 (1)	1,96 (1)
			1,96 (1)	1,98 (1)
Cu(CH ₃ COO) ₂ .C ₅ H ₅ N, forme α (ii)	2,645 (2)	2,186 (8)	1,978 (8)	1,98 (1)
			1,965 (7)	
			1,948 (8)	
			1,928 (8)	
Cu(CH ₃ COO) ₂ .C ₅ H ₅ N, forme β (iii)	2,630 (3)	2,122 (9)	1,98 (1)	
			1,97 (1)	
			1,98 (1)	
			1,98 (1)	

Références: (i) cette étude, (ii) Hanic, Stempelova & Hanicova (1964), (iii) Barclay & Kennard (1961).

Nous avons rassemblé dans le Tableau 4 les distances trouvées dans ces trois structures pour l'environnement du cuivre.

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5,6,7,8-Tetrahydro-4H-isoxazolo[4,5-d]azepin-3-ol Monohydrate, a Structural Analogue of GABA

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Abstract. C₇H₁₀N₂O₂.H₂O, *M* = 172.19; monoclinic, *P*2₁/*c*; *a* = 6.809 (3), *b* = 7.475 (2), *c* = 15.771 (4) Å, β = 95.58 (2)°; *Z* = 4, *D_m*(flotation) = 1.43, *D_x* = 1.432 g cm⁻³. The title compound has the expected zwitterionic structure. The isoxazole ring is planar, and the seven-membered ring adopts a chair conformation. The crystal structure is stabilized by a network of hydrogen bonds.

Introduction. Platelet crystals of C₇H₁₀N₂O₂.H₂O (Krogsgaard-Larsen & Hjeds, 1974) were obtained by slowly evaporating an aqueous solution at room temperature. X-ray intensities were measured with a Nonius three-circle automatic diffractometer and graphite-monochromated Mo *K*α (λ = 0.71069 Å) radiation. The ω-scan technique with a scan speed of 1.2° min⁻¹ was employed. The crystal (0.28 × 0.20 ×

0.11 mm) was sealed in a glass capillary and oriented with the *a* axis parallel to the φ axis of the goniostat. Of the 1380 independent reflexions measured in the range 2.5 ≤ θ ≤ 26.0°, 677 had net intensities greater than 3.0σ(*I*), where σ(*I*) is the standard deviation from counting statistics. These were regarded as observed reflexions and used in the refinement procedure. Lorentz and polarization corrections were applied, but no absorption correction was made [μ(Mo *K*α) = 1.22 cm⁻¹]. The unit-cell parameters were refined by least-squares techniques using the 2θ angles measured on the diffractometer from 39 reflexions.

The positions of the non-hydrogen atoms were determined by direct methods and refined by full-matrix least-squares techniques [X-RAY system (1972)]. A difference Fourier synthesis phased on the structural parameters so obtained revealed all 12 H atoms. The

positions of the H atoms bonded to C and N atoms were in accordance with calculated positions. The final refinement was carried out by varying an overall scale factor, atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms and atomic coordinates for the H atoms of the water molecule. The positional parameters of the remaining H atoms were fixed at calculated positions (C-H=1.0 Å; N-H=0.9 Å). The thermal parameters for all the H atoms were fixed at isotropic values corresponding to those of the non-hydrogen atoms to which they were attached. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight applied to each observation was $w = 1.0/[1.2 + 3\sigma^2(F_o) + 0.40/\sin \theta - 0.40|F_o| + 0.015|F_o|^2]$. The final R is 0.053 ($R_w = 0.048$). The X-ray atomic scattering factors used were those of Cromer & Mann (1968) for O, N and C and of Stewart, Davidson & Simpson (1965) for H. Table 1 lists the final atomic coordinates and thermal parameters.*

Discussion. Muscimol (5-aminomethyl-3-isoxazolol) is a semi-rigid analogue of γ -aminobutyric acid (GABA). A correlation of the structures with the corresponding activities of a series of compounds structurally related to muscimol has been made (Krogsgaard-Larsen & Johnston, 1975; Krogsgaard-Larsen, Johnston, Curtis, Game & McCulloch, 1975). The title compound did not inhibit GABA uptake and showed no activity with respect to GABA receptors. An unexpected finding, however, was that the compound antagonized the depressant action of glycine, although the effect was weak when compared with that of the specific antagonist strychnine (Curtis, Duggan & Johnston, 1971).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31935 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

A wide variety of compounds are known to be glycine antagonists (Curtis & Johnson, 1974).

The conformation of the title compound in the crystalline state is shown in Fig. 1, in which the num-

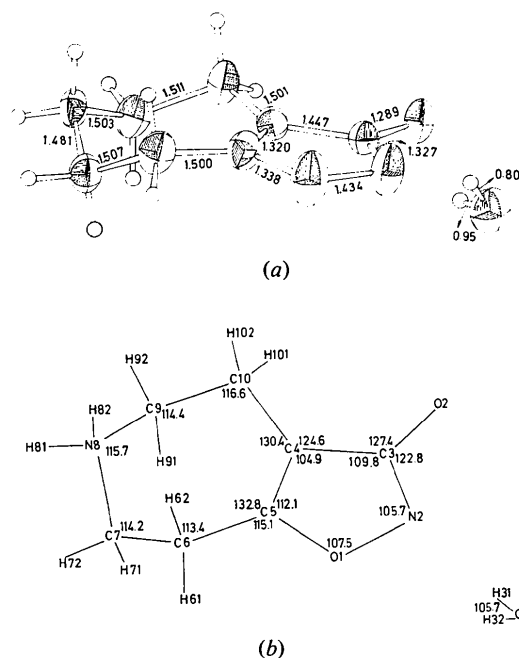


Fig. 1. (a) Bond lengths (Å) between non-hydrogen atoms. The intramolecular distances N(8)···O(2), N(8)···N(2) and N(8)···O(1) are 5.402, 5.158 and 4.385 Å respectively, e.s.d.'s are 0.004–0.007 Å. Bond lengths involving H atoms of the water molecule, e.s.d.'s are 0.05 Å. Thermal ellipsoids for non-hydrogen atoms are scaled to 50% probability; H atoms are represented as spheres of arbitrary radius. The molecule is viewed along a^* . (b) The numbering of the atoms and bond angles ($^\circ$) involving non-hydrogen atoms, e.s.d.'s are 0.3–0.4 $^\circ$. The valency angle of the water molecule, e.s.d. is 5 $^\circ$. The molecules are rotated -30° about the c axis relative to the molecule in (a) (Johnson, 1965).

Table 1. Atomic coordinates, vibrational-tensor components ($U_{ij} \times 10^3$) for non-hydrogen atoms and isotropic values ($U \times 10^3$) for the hydrogen atoms

The estimated standard deviations are given in parentheses. The U_{ij} values (\AA^2) correspond to the temperature factor expression:

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.4848 (5)	0.1644 (5)	0.2180 (2)	39 (2)	81 (3)	35 (2)	15 (2)	13 (2)	-4 (2)
N(2)	0.3741 (6)	0.1961 (6)	0.1373 (2)	43 (2)	67 (3)	29 (2)	11 (2)	6 (2)	-3 (2)
O(2)	0.0619 (4)	0.3015 (5)	0.0974 (2)	39 (2)	53 (2)	22 (1)	2 (2)	0 (1)	-2 (1)
C(3)	0.2004 (6)	0.2583 (6)	0.1553 (3)	38 (2)	29 (3)	27 (2)	-1 (2)	10 (2)	-1 (2)
C(4)	0.1971 (6)	0.2718 (6)	0.2467 (2)	33 (2)	31 (3)	25 (2)	-2 (2)	3 (2)	2 (2)
C(5)	0.3717 (6)	0.2134 (6)	0.2788 (2)	33 (2)	40 (3)	27 (2)	-1 (2)	7 (2)	-2 (2)
C(6)	0.4660 (6)	0.1939 (7)	0.3683 (3)	32 (2)	51 (3)	33 (2)	11 (2)	2 (2)	-7 (2)
C(7)	0.3231 (7)	0.1391 (6)	0.4307 (2)	42 (3)	41 (3)	21 (2)	3 (2)	-2 (2)	-2 (2)
N(8)	0.1657 (5)	0.2717 (5)	0.4410 (2)	33 (2)	39 (2)	20 (2)	-9 (2)	6 (1)	1 (2)
C(9)	-0.0081 (6)	0.2662 (7)	0.3746 (3)	25 (2)	52 (3)	27 (2)	3 (2)	5 (2)	-6 (2)
C(10)	0.0297 (6)	0.3487 (7)	0.2902 (3)	32 (2)	46 (3)	27 (2)	9 (2)	4 (2)	-1 (2)
O(3)	0.7123 (6)	0.1298 (5)	0.0485 (2)	44 (2)	50 (2)	40 (2)	6 (2)	14 (2)	-3 (2)
H(31)	0.606 (8)	0.149 (7)	0.082 (3)	45					
H(32)	0.802 (8)	0.187 (7)	0.071 (3)	45					

bering of the atoms and some distances and angles are also indicated.

The isoxazole ring is planar within the limits of experimental error. The exocyclic oxygen atom O(2) is situated in the least-squares plane through the isoxazole ring, while C(6) and C(10) are at distances of ± 0.03 and ± 0.08 Å respectively from this plane. The seven-membered ring adopts a chair conformation, with an approximate mirror plane passing through N(8) and the midpoint of the C(4)–C(5) bond. The torsion angles in this ring are given in Table 2. They show some deviations from the torsion angles derived from force-field calculations for the C_7 -chair conformer of cycloheptene (Ermer & Lifson, 1973).

The packing of the molecules in the crystals is

stabilized by a system of hydrogen bonds. All H atoms which are covalently bonded to N and O atoms are utilized in the formation of hydrogen bonds (Fig. 2).

The zwitterions are situated in puckered layers about the *c* glide planes at $b = \frac{1}{4}$ and $\frac{3}{4}$. The *c* glide plane-related zwitterions within each layer are bound head-to-tail by the hydrogen bond N(8)–H(81)···O(2) thereby forming infinite chains in the *c* direction. These chains are connected in the *a* direction *via* the water molecules, the hydrogen bonds being O(3)–H(31)···N(2) and O(3)–H(32)···O(2). The layers are interlinked in the *b* direction by the hydrogen bond N(8)–H(82)···O(3).

Hydrogen-bond distances and angles are given in Table 3. All other intermolecular contacts correspond to van der Waals interactions.

Table 2. Torsion angles with the estimated standard deviations in parentheses

C(9)–C(10)–C(4)–C(5)	∓ 37.9 (7) ^o
C(10)–C(4)–C(5)–C(6)	± 3.0 (9)
C(4)–C(5)–C(6)–C(7)	± 36.1 (8)
C(5)–C(6)–C(7)–N(8)	∓ 63.6 (5)
C(6)–C(7)–N(8)–C(9)	± 82.2 (4)
C(7)–N(8)–C(9)–C(10)	∓ 76.6 (5)
N(8)–C(9)–C(10)–C(4)	± 57.5 (5)

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Table 3. Hydrogen-bond distances and angles with the estimated standard deviations in parentheses

Symmetry code				
(i)	$1+x, y, z$	(iii)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	
(ii)	$x, \frac{1}{2}-y, \frac{1}{2}+z$			
<i>A</i> –H··· <i>B</i>	<i>A</i> –H	H··· <i>B</i>	<i>A</i> ··· <i>B</i>	\angle AHB
O(3)–H(31)···N(2)	0.95 (5) Å	1.91 (6) Å	2.854 (6) Å	173 (4) ^o
O(3)–H(32)···O(2) ⁱ	0.80 (5)	1.97 (5)	2.748 (5)	164 (5)
N(8)–H(81)···O(2) ⁱⁱ	0.90	1.79 (5)	2.686 (4)	172 (5)
N(8)–H(82)···O(3) ⁱⁱⁱ	0.90	1.92 (5)	2.803 (5)	168 (5)

The e.s.d.'s of the hydrogen-atom positions which were not refined have been assumed to be the same as those of the hydrogen-atom positions which were refined, *i.e.* H(31) and H(32).

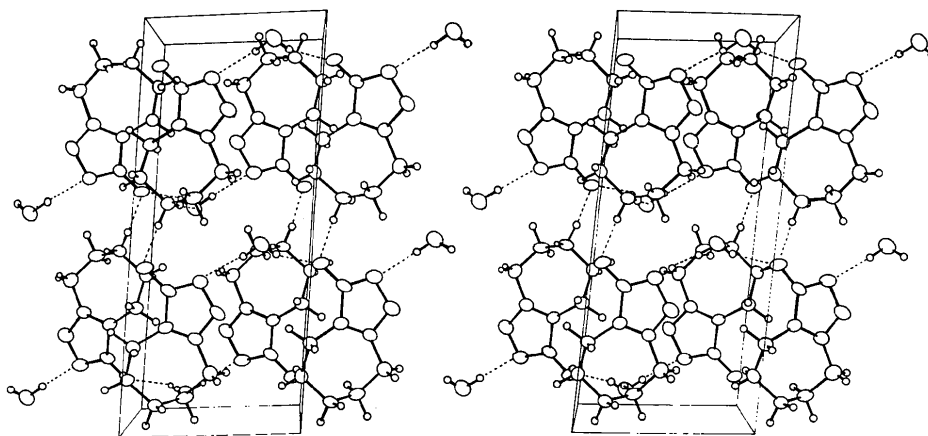


Fig. 2. Stereo diagram illustrating the molecular packing. The view is down *b*, with *a* → and *c* ↓. Hydrogen bonds are drawn with broken lines (Johnson, 1965).

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Dimethyl 8-*exo*-Phenylbicyclo[5.1.0]octa-2,4-diene-8-phosphonate

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Abstract. $C_{16}H_{19}O_3P$, monoclinic, $P2_1/c$; $a=13.651$ (9), $b=12.406$ (8), $c=9.037$ (5) Å, $\beta=91.25$ (2)°; $Z=4$, $M=290.28$, $D_x=1.261$ g cm⁻³. The highly strained nature of the bicyclic ring system becomes evident from very short C–C single bonds and a torsion angle around one double bond of 29°.

Introduction. The compound is obtained by photolysis or thermolysis of dimethyl (diazobenzyl)phosphonate in excess cycloheptatriene. It is the minor product of the 1:1 addition of the intermediately formed carbene to the solvent. Moreover, there exists a photochemical equilibrium with the analogous *endo*-phenyl isomer

(Maas, 1976) which is the major product of the direct carbene addition to cycloheptatriene. Crystals for X-ray analysis were obtained by sublimation of the crude product and recrystallization from ether (m.p. 129°C).

Systematic extinctions on Weissenberg and precession photographs ($h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$) indicated space group $P2_1/c$. Intensities from a crystal fragment, $0.24 \times 0.14 \times 0.09$ mm, were collected on a Siemens diffractometer (AED) with Ni-filtered Cu $K\alpha$ radiation and a scintillation counter. With a $\theta/2\theta$ -scan and the five-values method, 1688 reflexions in the range $0 < \theta < 51.45^\circ$ were measured (scan speed 0.24 s/ 0.01°). Two control reflexions (900 and 080)

Table 1. Atomic coordinates and thermal parameters of the non-hydrogen atoms (all $\times 10^4$, e.s.d.'s are in parentheses)

The thermal ellipsoid is defined by $\exp [-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + \dots)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
P	3255 (1)	5788 (1)	6264 (1)	59 (1)	79 (1)	125 (1)	-13 (1)	-29 (2)	-7 (2)
O(1)	4021 (2)	6264 (3)	5195 (4)	99 (3)	104 (3)	204 (5)	-78 (4)	34 (6)	-40 (6)
O(2)	3726 (2)	4674 (2)	6693 (3)	77 (2)	99 (3)	221 (6)	16 (4)	-100 (6)	33 (6)
O(3)	3056 (2)	6474 (3)	7527 (3)	82 (2)	139 (3)	148 (5)	-13 (5)	-41 (5)	-94 (7)
C(1)	1197 (4)	4900 (5)	7461 (5)	86 (4)	146 (5)	163 (8)	-39 (7)	46 (8)	-23 (11)
C(2)	445 (6)	5387 (7)	8079 (7)	210 (8)	248 (10)	193 (10)	11 (15)	162 (15)	-44 (17)
C(3)	-77 (4)	6283 (6)	7675 (6)	81 (4)	270 (10)	224 (10)	10 (10)	-19 (10)	-272 (16)
C(4)	247 (5)	7053 (6)	6775 (8)	140 (6)	173 (7)	324 (13)	99 (11)	-41 (14)	-182 (16)
C(5)	1109 (4)	7045 (4)	5862 (6)	80 (3)	125 (5)	212 (9)	61 (7)	-71 (9)	-99 (11)
C(6)	1292 (3)	6009 (4)	5052 (6)	66 (3)	105 (4)	138 (6)	33 (6)	-49 (7)	-57 (8)
C(7)	1318 (3)	4966 (4)	5822 (5)	73 (3)	107 (4)	136 (7)	-32 (6)	-9 (7)	-52 (9)
C(8)	2249 (3)	5373 (3)	5111 (4)	55 (3)	76 (3)	116 (5)	-2 (5)	-20 (6)	-4 (7)
C(9)	2540 (3)	4847 (3)	3678 (4)	55 (3)	76 (3)	118 (6)	1 (5)	-29 (6)	-17 (7)
C(10)	2626 (3)	5455 (3)	2398 (4)	69 (3)	77 (4)	134 (6)	4 (5)	-13 (7)	1 (7)
C(11)	2861 (3)	4981 (4)	1069 (5)	82 (3)	111 (4)	128 (6)	-19 (6)	-6 (7)	6 (9)
C(12)	3036 (4)	3889 (4)	1010 (5)	96 (4)	109 (4)	152 (7)	1 (7)	16 (8)	-57 (9)
C(13)	2975 (5)	3276 (4)	2265 (5)	106 (4)	77 (4)	207 (8)	27 (6)	0 (9)	-59 (9)
C(14)	2723 (3)	3748 (3)	3606 (5)	91 (4)	71 (4)	168 (7)	26 (6)	-12 (8)	-10 (8)
C(15)	4371 (5)	7341 (4)	5199 (7)	145 (5)	105 (5)	297 (12)	-77 (9)	-42 (13)	12 (13)
C(16)	4635 (4)	4683 (5)	7550 (6)	78 (4)	158 (6)	215 (9)	38 (8)	-82 (9)	53 (12)