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Hydrogen-Bond Motifs of Carboxylic Acids: the β -Form of Monochloroacetic Acid

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Abstract. $C_2H_3O_2Cl$, monoclinic, $P2_1/c$; $a = 4.635$ (10), $b = 12.974$ (24), $c = 6.686$ (16) Å, $\beta = 107.93$ (19)°; $Z = 4$, $D_c = 1.647$ g cm⁻³. The structure consists of cyclic dimers formed by hydrogen bonding across centres of symmetry.

Introduction. As part of a programme to study the monochloroacetic acid, the structure of the stable α -form has been determined (Kanters & Roelofsen, 1976). The α -form exhibits a hydrogen-bond motif that has not so far been observed in carboxylic acids in the solid state (Leiserowitz, 1976). The motif consists of centrosymmetric hydrogen-bonded tetramers and may be looked upon as an intermediate form of the polymeric structure of acetic acid (Nahringbauer, 1970) and formic acid (Holtzberg, Post & Fankuchen, 1953) and the commonly observed cyclic dimer structure.

From IR and Raman studies of the metastable β -form of monochloroacetic acid (Sinha, Katon & Jakobsen, 1975) it was concluded that this modification adopts the usual cyclic hydrogen-bonded dimer type. This paper describes the determination of the crystal structure of the β -form.

Crystals were prepared by the method described by Aumeras & Minangoy (1948). This consists of heating the melt of the α -form (m.p. 64°C) to 75°C and keeping the melt at that temperature for 30 min to ensure that no traces of the stable α -form are present. After allowing the melt to cool slowly at a rate of 1°C/20 min, rapid crystallization of tablets of the β -form takes place at 54°C. Oscillation and Weissenberg photographs indicated that the crystals were monoclinic, with systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$, determining the space group as $P2_1/c$. It appeared that the crystals thus prepared were twinned.

Table 1. Fractional coordinates ($\times 10^4$ for Cl, C and O; $\times 10^3$ for H) and anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms

The estimated standard deviations are given in parentheses and refer to the last decimal position of respective values. The anisotropic temperature factor is of the form $\exp[-2\pi^2(a^{*2}h^2U_{11} + \dots + 2b^*c^*klU_{23})]$.

	x	y	z	U_{11} or B (Å ²)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	2007 (3)	3356 (1)	1156 (2)	479 (8)	662 (10)	414 (7)	-5 (7)	28 (6)	143 (6)
O(1)	-2634 (9)	4077 (3)	-4566 (6)	440 (23)	596 (25)	416 (20)	-146 (19)	6 (17)	97 (18)
O(2)	1832 (8)	4638 (3)	-2507 (6)	409 (21)	528 (23)	425 (19)	-96 (17)	72 (16)	53 (17)
C(1)	-457 (10)	4131 (4)	-2800 (7)	289 (25)	321 (23)	373 (24)	34 (18)	91 (19)	-44 (18)
C(2)	-1178 (13)	3509 (5)	-1108 (8)	407 (30)	522 (32)	378 (26)	-101 (24)	63 (22)	6 (23)
H(1)	-293 (12)	391 (4)	-63 (8)	3.3					
H(2)	-224 (12)	292 (4)	-160 (8)	3.3					
H(3)	-226 (13)	444 (4)	-536 (9)	3.7					

However, the orientation of the twins is such that the reflexions are only slightly separated in the direction of \mathbf{a}^* . A crystal $0.6 \times 0.5 \times 0.5$ mm was sealed in a capillary tube to prevent sublimation. After determination of the cell dimensions, a set of 1590 intensities ($\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$) was collected on a computer-controlled Nonius CAD-3 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) by the ω -scan technique. A large scan angle, up to 4° , was used to allow measurement of possibly present twinned peaks. The equivalent reflexions were averaged to give 806 independent intensities of which 616 were $> 2.5\sigma(I)$. Lorentz and polarization corrections, but no absorption correction [$\mu(\text{Mo } K\alpha) = 8.0 \text{ cm}^{-1}$], were applied.

The structure was solved by direct phasing methods based on the tangent formula of Karle & Hauptman (1956) with the *MULTAN* program of the X-RAY system (1972). An *E* map revealed the positions of the non-hydrogen atoms. Isotropic block-diagonal least-squares refinement followed by anisotropic refinement and a difference synthesis revealed the positions of the H atoms. Three more cycles of anisotropic full-matrix refinement with constant *B*'s (equal to those of the carrier atoms) for the H atoms gave an *R* of 0.058 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). The weighted *R* was 0.058 $\{w = \sigma^{-2}(F_o) \text{ and } R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$. The goodness-of-fit defined as $[\sum w(|F_o| - |F_c|)^2 / (m - s)]^{1/2}$, where *m* is the number of observations and *s* the number of parameters, was 0.85. The average shift in the last cycle was 0.01σ for the heavy and 0.08σ for the H atoms.

Two reflexions (100 and 200) with a large disagreement were excluded from the refinement. The scattering factors for Cl, C and O were those of Cromer & Mann (1968), and for H those of Stewart, Davidson & Simpson (1965). In Table 1 the final positional and thermal parameters are listed.†

Discussion. The bond distances and angles (Table 2) compare well with the corresponding values for the α -form (Kanters & Roelofsen, 1976). The short C-C

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31929 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond distances (\AA) and angles ($^\circ$) of the β -form of monochloroacetic acid

Estimated standard deviations are given in parentheses.

C(2)-Cl	1.770 (5)	C(1)-C(2)-Cl	112.5 (4)
C(2)-C(1)	1.508 (8)	C(2)-C(1)-O(1)	111.4 (4)
C(1)-O(1)	1.297 (5)	C(2)-C(1)-O(2)	123.6 (4)
C(1)-O(2)	1.212 (6)	O(1)-C(1)-O(2)	124.9 (5)
C(2)-H(1)	1.09 (6)	H(3)-O(1)-C(1)	109 (4)
C(2)-H(2)	0.91 (5)	H(1)-C(2)-Cl	107 (2)
O(1)-H(3)	0.77 (6)	H(2)-C(2)-Cl	115 (3)
		H(1)-C(2)-C(1)	109 (3)
		H(2)-C(2)-C(1)	113 (4)
		H(1)-C(2)-H(2)	98 (5)

Table 3. Comparison of the geometries of the dimer and tetramer motifs of halogenated acetic acids, distances in \AA and angles in degrees

Ref.	Estimated standard deviations are given in parentheses.										Distance of halogen atom to CCOO plane
	O...O	O-H...O	C-O(H)...O	C=O...O	C-O	O-H	O=C-O	C-O-H	Dihedral angle		
1	2.64 (1)	151 (4)	111.9 (5)	1.22 (1)	1.31 (1)	1.00 (7)	123.9 (5)	113 (4)	0.3	0.00	
2	2.697 (3)	175 (2)	105.9 (3)	1.200 (3)	1.316 (3)	0.83 (4)	124.4 (3)	108 (2)	0.8	0.01	
3	2.706 (4)	168 (2)	106.8 (3)	1.204 (4)	1.313 (3)	0.99 (4)	123.7 (3)	113 (2)	20.3	0.56	
4	2.682 (5)	173 (4)	112.8 (6)	1.212 (6)	1.297 (5)	0.77 (6)	124.9 (5)	109 (4)	13.8	0.35	
	2.642 (12)	133 (8)	114.2 (8)	1.190 (12)	1.314 (13)	0.95 (11)	122.9 (8)	94 (8)	8.5	0.24	
	2.655 (9)	162 (9)	113.0 (9)	1.227 (8)	1.295 (9)	1.08 (14)	123.9 (9)	102 (8)	22.0	0.68	

(1) Fluoroacetic acid, Kanters & Kroon (1972); (2) α -form of chloroacetic acid, Kanters & Roelofsen (1976); (3) β -form of chloroacetic acid, this paper; (4) two modifications of bromoacetic acid, Leiserowitz & von der Brück (1975).

distance (1.508 Å) is also found in the α -form, as well as in other substituted acetic acids (Kanters & Roelofsen, 1976). The conformation is synplanar and the dihedral angle $C(2)-C(1)-O(1)-O(2)/C(1)-C(2)-Cl$ (13.8°) is intermediate between those in the two independent molecules of the α -form, 0.8 and 20.3° respectively. From Fig. 1, a projection of the structure along a , it can be seen that the molecules are arranged as cyclic centrosymmetric dimers by hydrogen bonding of the carboxyl groups. This dimer structure is in accordance with the model proposed by Sinha, Katon & Jakobsen (1975) on the basis of the lack of coincidence in the IR and Raman spectra. Though the cyclic dimer structure nearly always represents the stable form of carboxylic acids (Leiserowitz, 1976) and particularly of the closely related fluoroacetic acid (Kanters & Kroon, 1972), and two modifications of bromoacetic acid (Leiserowitz & von der Brück, 1975), it nevertheless

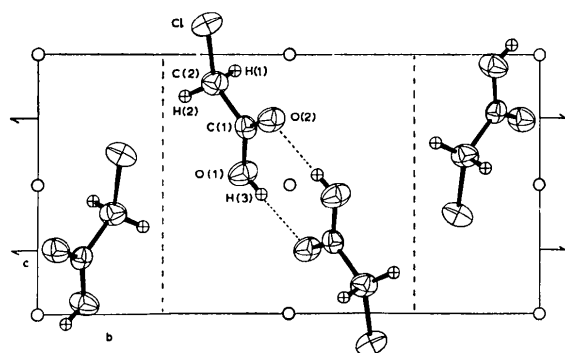


Fig. 1. Projection of the structure along a . Hydrogen bonds are denoted by dashed lines.

turns out that the stable form of chloroacetic acid adopts the unusual tetramer motif (Kanters & Roelofsen, 1976). In Table 3 characteristic data of dimer structures in crystals of halogenated acetic acids are given together with the data of the tetramer structure of the α -form of chloroacetic acid. The hydrogen-bond distances in both the α - and β -forms are larger than those observed in crystals of dimerized acids (average 2.65 Å). The hydrogen-bond donor and acceptor angles of the β -form agree well with the corresponding angles in the other dimers, whereas the α -form shows large deviations.

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Études des Propionates Métalliques.

VI. Détermination de la Structure Cristalline du Bis-propionato Cuivre(II) Pyridine

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Abstract. $Cu(CH_3CH_2COO)_2 \cdot C_5H_5N$, triclinic, $P\bar{1}$, $a = 16.204$ (9), $b = 8.442$ (5), $c = 11.618$ (7) Å, $\alpha = 103.9$ (1), $\beta = 121.0$ (1), $\gamma = 90.4$ (1) $^\circ$; $Z = 4$, $V = 1308$ Å 3 , $d_{exp}(25^\circ C) = 1.45$ (3), $d_{calc} = 1.45$ g cm $^{-3}$, $\mu_l(Mo K\alpha) = 21.21$ cm $^{-1}$, $\mu_r(Mo K\alpha) = 0.7$. The crystal has two independent binuclear units with carboxyl bridges and Cu–Cu bonds = 2.642 (2) and 2.619 (2) Å.

Introduction. Ce travail se situe dans le cadre d'une étude structurale et thermochimique d'une série de

solvates du propionate de cuivre présentant une structure dimère avec une interaction cuivre–cuivre.

Nous avons commencé cette étude par la détermination des structures cristallines du propionate de cuivre solvaté par la β picoline (Borel, Busnot & Leclaire, 1976a; Borel & Leclaire, 1976) et l' α picoline (Borel, Busnot & Leclaire, 1976c); nous la poursuivons par la structure du bis-propionato cuivre(II) pyridine.

Par action de l'acide propionique sur le carbonate de cuivre(II) dans la pyridine, on obtient par évapora-