

cultural College of Sweden, Uppsala, for placing the NMR instrument at their disposal.

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On the Structures of Two Crystalline Forms of Oxydiacetic Acid

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The structure of the oxydiacetate group has been investigated in several compounds. It has been determined as hydrogen oxydiacetate ion in alkali salts,^{1,2} and as oxydiacetate ion in cadmium³ and lanthanoid⁴ compounds. In these structures the ligand is planar, except in one of the three known cadmium oxydiacetate phases.³ In the alkali compounds, hydrogen bond systems with very short hydrogen bonds were found.^{1,2} We considered it therefore to be of interest to examine the free acid especially with regard to planarity and hydrogen bonds.

From aqueous solutions of oxydiacetic acid two different crystalline phases, one orthorhombic and one monoclinic, are formed side by side at room temperature. In order to determine space groups and preliminary cell dimensions, rotation and Weissenberg photographs were taken for both phases. Some important crystal data are summarized in Table 1. The orthorhombic crystals are efflorescent at room temperature. From the observed density, 1.54 g cm⁻³, and the cell volume given in Table 1, it is concluded that there is at least one water of crystallization in this compound.

Powder photographs for the monoclinic phase were obtained from a Guinier-Hägg camera with CuK α_1 radiation and aluminium (cubic $a=4.04934$ Å) as internal standard. Least-squares refinement of the data gave the accurate cell constants shown in Table 1.

Table 1. Crystal data for the two phases of oxydiacetic acid.

Space group	Monoclinic <i>C2/c</i>	Orthorhombic <i>Pna2₁</i> or <i>Pnam</i>
<i>a</i>	9.706(2) Å	7.52 Å
<i>b</i>	3.941(1)	8.24
<i>c</i>	15.027(2)	10.84
β	104.79(2)°	—
<i>V</i>	555.75 Å ³	671 Å ³
<i>Z</i>	4	4

Powder photographs of the orthorhombic phase, showed, among other lines, also those characteristic of the monoclinic phase. The orthorhombic crystals are thus rather quickly transformed into the monoclinic phase, when powdered. For this reason we have not been able to refine the orthorhombic cell constants.

So far we have determined the structure of the monoclinic phase only. Three-dimensional intensity data have been collected by the use of the Weissenberg multiple film technique with CuK α radiation. The number of observed, independent reflexions was 396. The method of symbolic addition was used (GAASA) for the structure determination. The systematic extinctions were consistent with the space groups *C2/c* (No. 15) and *Cc* (No. 9). The *E* statistics were decidedly in favour of the centrosymmetrical space group *C2/c*.

The positions of the oxygen and carbon atoms were obtained from the *E* map. It

turned out that the ether oxygen occupied the special position 4(e), and thus only one-half of the other atoms in the molecule were independent and situated in 8(f). A least-squares refinement of the preliminary coordinates, followed by a difference Fourier synthesis with $\sin \theta/\lambda \leq 0.5$ (\AA^{-1}), gave the positions of the hydrogen atoms in the methylene group. The hydrogen atom in the carboxyl group involved in the hydrogen bonding could not be located, however.

The structure was refined isotropically by least-squares methods, the temperature factors for the hydrogen atoms being fixed to 5.0 \AA^2 . A difference synthesis at this stage indicated anisotropic temperature vibrations for the non-hydrogen atoms. A final anisotropic least-squares refinement, with $B = 5.0$ (\AA^2) for the hydrogen atoms, resulted in a weighted R -value of 0.081. The weights used in these calculations were assigned according to Cruickshank. The atomic parameters are given in Tables 2 and 3.

Table 2. Atomic coordinates with standard deviations ($\times 10^4$).

Atom	x	y	z
O(1)	0	4832(10)	2500
O(2)	-650(3)	2325(8)	4032(2)
O(3)	1416(3)	-401(8)	4468(2)
C(1)	1029(4)	2830(12)	3114(2)
C(2)	511(3)	1581(10)	3918(2)
H(1)	2057(92)	4104(250)	3451(70)
H(2)	1091(96)	432(250)	2838(75)

A schematic picture of the planar oxydiacetate ion is shown in Fig. 1, and a stereoscopic view of the structure of monoclinic oxydiacetic acid in Fig. 2.

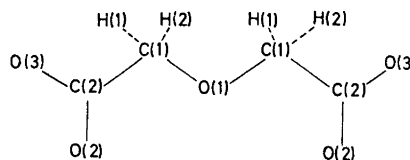


Fig. 1. A schematic picture of the oxydiacetate ion.

As seen from Fig. 2, the molecule is twisted about the ether oxygen O(1), so that the O(2) atoms are *trans* to each other. The non-hydrogen atoms in the independent half of the molecule are coplanar (Table 4), and the angle between

Table 4. Least-squares plane for the oxydiacetic molecule and distances of atoms from this plane.

Atoms defining plane	
O(1), O(2), O(3), C(1), C(2)	
Equation	
$-0.279x - 0.806y - 0.522z + 3.182 = 0$	
Displacement from the plane.	
O(1)	0.019 \AA
O(2)	-0.005
O(3)	0.017
C(1)	-0.023
C(2)	-0.009

the two ligand halves is 72° . The interatomic distances and angles given in Table 5 agree very well with those found in the alkali hydrogen oxydiacetates.^{1,2}

Table 3. Anisotropic thermal parameters with standard deviations ($\times 10^4$). The form of the temperature factor is $\exp(-\beta_{11}h^2 - \dots - 2\beta_{12}hk - \dots)$; the root-mean square components R_i ($\times 10^3$) in \AA of thermal displacement along the ellipsoid axes are also listed.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
O(1)	96(5)	230(33)	19(1)	0	2(2)	0	216	135	141
O(2)	82(4)	507(30)	28(1)	57(7)	13(2)	29(4)	224	156	179
O(3)	84(3)	456(29)	27(1)	46(7)	9(1)	27(5)	213	149	190
C(1)	67(4)	245(35)	21(1)	-16(9)	2(2)	0(5)	186	135	146
C(2)	60(3)	236(34)	15(1)	-14(7)	8(2)	-22(4)	166	106	152

Table 5. Interatomic distances and angles for monoclinic oxydiacetic acid.

Distances	Å	Angles	°
O(1)–C(1)	1.415(5)	C(1)–O(1)–C(1)	112.2(4)
C(1)–C(2)	1.505(5)	O(1)–C(1)–C(2)	112.3(3)
C(2)–O(2)	1.218(4)	C(1)–C(2)–O(2)	123.0(3)
C(2)–O(3)	1.302(4)	C(1)–C(2)–O(3)	113.4(3)
O(2)–O(3)	2.221(4)	O(2)–C(2)–O(3)	123.6(3)
C(1)–H(1)	1.12(9)	O(1)–C(1)–H(1)	116(5)
C(1)–H(2)	1.04(10)	O(1)–C(1)–H(2)	111(6)
		C(2)–C(1)–H(1)	103(5)
		C(2)–C(1)–H(2)	95(6)
		H(1)–C(1)–H(2)	117(7)

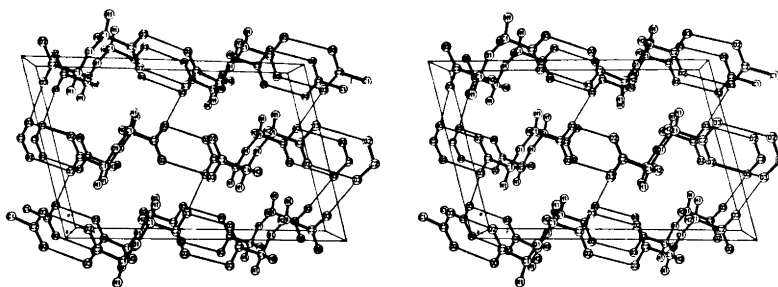


Fig. 2. A stereoscopic drawing of the structure of the monoclinic oxydiacetic acid.

As seen from Table 5, the distances C(2)–O(2) and C(2)–O(3) are 1.218(4) and 1.302(4) Å, respectively. The hydrogen atom in the carboxyl group should thus be closer to O(3) than to O(2). The structure may be described in two different ways, depending on the position of the carboxyl hydrogen atom. If it is situated on a line between the atoms O(2) and O(3), which are 2.65 Å apart, infinite chains are formed along the *c*-axis; the chains are held together by van der Waals forces. On the other hand, the distances O(3)–O(2) and O(3)–O(3), which are 2.65 and 2.83 Å, respectively, might indicate a bifurcated hydrogen bond, with the hydrogen atom situated within the triangle formed by the atoms O(3), O(3), and O(2). If this is the case, the structure is hydrogen-bonded in three dimensions.

We will later try to find the position of the hydrogen atom in the carboxyl group by the use of a more refined technique, and so be able to decide which one of the two models is the correct one.

For the orthorhombic phase, three-dimensional X-ray intensity data have been collected as for the monoclinic phase. Possible space groups are *Pnam* (No. 62) and *Pna2₁* (No. 33), and the *E* statistics indicate *Pna2₁* as the more probable one. Attempts to solve the structure of this compound are being continued.

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