THE CRYSTAL STRUCTURE OF MAGNESIUM ACETATE-TETRAHYDRATE $Mg(CH_3COO)_2.4H_2O$

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1. INTRODUCTION

RECENTLY Van Niekerk and Schoening[1] have studied the structures of a number of metal acetates. They have stated that direct metal bonds exist in some of these compounds. Magnesium acetate tetrahydrate belongs to the same group as those studied by Niekerk *et al.*, and the present paper gives a report of the investigation of its structure by X-rays.

2. EXPERIMENTAL

The crystals of magnesium acetate were obtained from its aqueous solution by slow evaporation. The crystals were needle-shaped, the long axis being the *c*-axis. The unit cell dimensions, as determined from rotation and Weissenberg photographs, are

$$a = 4{\cdot}75\ \text{Å},\quad b = 11{\cdot}79\ \text{Å},\quad c = 8{\cdot}52\ \text{Å}\quad \text{and}\quad \beta = 94^\circ\ 54'.$$

The axial ratios $a:b:c = 0{\cdot}402 : 1 : 0{\cdot}719$ are in good agreement with the previously reported morphological values $a:b:c = 0{\cdot}403 : 1 : 0{\cdot}7128$ and $\beta = 95^\circ\ 37'$ (Groth[2]). Taking the density to be 1·453 (*Hand-book of Chemistry and Physics*) the number of molecules per unit cell is 1·98, *i.e.*, 2. There were no systematic absences in the $h\,k\,l$ reflections showing that the unit cell is primitive. The list of reflecting planes reveals that $0\,k\,0$ is absent when k is odd, and $h\,0\,l$ when l is odd. The space-group is therefore $C_{2h}^5 - P2_1/c$.

Using the multiple film technique, the zero layer Weissenberg photographs were taken on suitable crystal specimens rotating about the *a*- and *b*-axes using Cu-K_α radiation. The intensities of the reflections were estimated visually and corrected in the usual way for the Lorentz and polarisation factors. In view of the small size of the crystals used no corrections were considered necessary for absorption and extinction.

3. DETERMINATION OF THE STRUCTURE

Since the general point position in the $P2_1/c$ is four-fold and as the unit cell contains only two molecules, it follows that the magnesium atoms must be on symmetry centres. The magnesium position was therefore taken at (0, 0, 0). Since the cell dimensions of magnesium acetate and nickel acetate are almost identical, and since they belong to the space-group C_{2h}^5 with the metal atoms at special positions, the signs of the structure factors of magnesium acetate were deduced from those for nickel acctate, taking into consideration the contribution due to the metal atoms. With the signs so obtained a trial Fourier projection on the *bc* plane was made. The projection thus obtained clearly showed the positions of all the atoms and the peaks were well resolved. The maxima were located for all the atoms by Booth's method,[3] and the *y* and *z* co-ordinates of the atoms were estimated. The process was repeated for the *ac* plane, and a Fourier projection was made. Figs. 1 and 2 give the Fourier projections on *bc* and *ac* planes respectively. From these projections the co-ordinates were estimated (Table I).

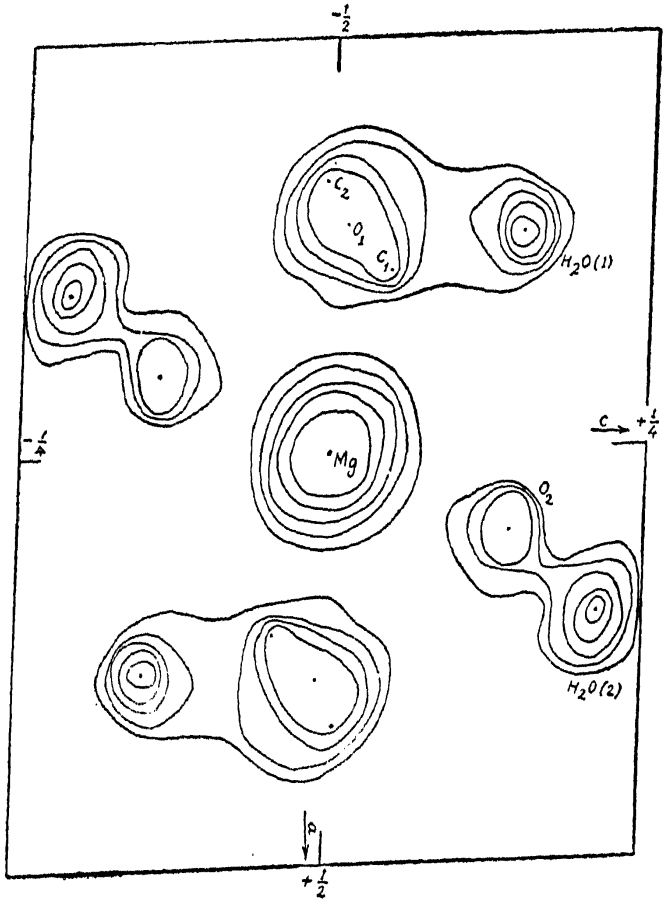

FIG. 1. Fourier projection of the electron density on (*ac*) plane.

With these co-ordinates, structure factors were calculated by allowing for the temperature corrections. The *f*-values for carbon were taken from

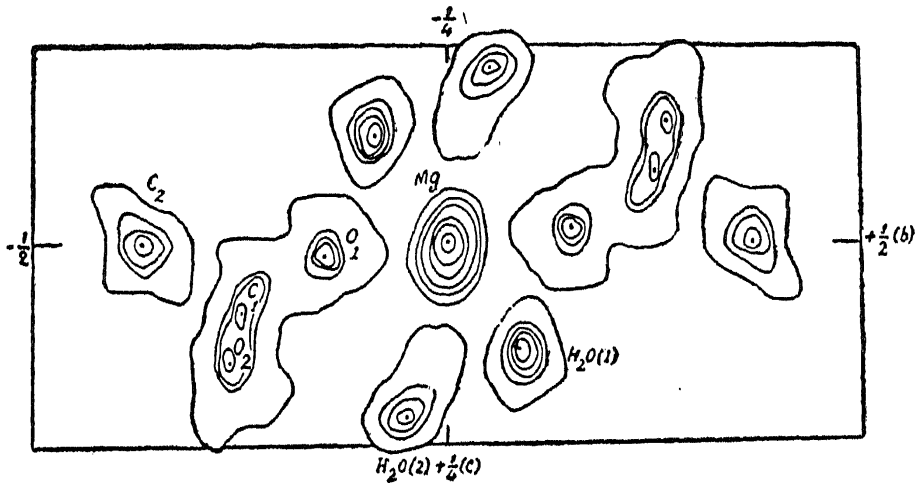

FIG. 2. Fourier projection of the electron density on (*bc*) plane.

TABLE I

Atomic parameters

	x	*y*	*z*
Mg	0·000	0·000	0·000
O_1	−0·250	−0·150	−0·015
O_2	0·067	−0·267	0·150
$H_2O_{(1)}$	−0·283	0·083	0·133
$H_2O_{(2)}$	0·200	−0·050	0·217
C_1	−0·183	−0·250	0·083
C_2	−0·300	−0·367	−0·001

Robertson,[4] for oxygen they were proportionately deduced from Robertsons's values, and for magnesium atom an isotropic temperature factor with B = 1·2 was used. In Table II, the calculated and observed structure. factor values are given. The agreement is good and the Reliability Factor R comes out to be 0·13 for [(0 *k l*)] zone and 0·21 for [(*h* 0 *l*)] zone. The bond length and the angles are given in Table III, which were deduced from the atomic co-ordinates given in Table I.

TABLE II

h	k	l	F_c	F_0	h	k	l	F_c	F_0	h	k	l	F_c	F_0
1	0	0	+45	35	0	4	5	+ 4	4	0	12	3	+ 2	4
2	0	0	+35	30	0	4	6	+ 2	6	0	12	4	− 1	3
3	0	0	+17	17	0	5	1	+ 8	11	0	12	5	+ 3	5
4	0	0	+34	26	0	5	2	+21	24	0	13	1	+ 7	5
5	0	0	+ 9	5	0	5	3	+14	19	0	13	5	+ 4	4
0	2	0	− 7	10	0	5	4	− 7	8	1	0	2	+30	24
0	4	0	+17	17	0	5	5	+13	13	1	0	4	+22	19
0	6	0	− 5	5	0	5	6	+ 4	6	1	0	6	+ 5	8
0	8	0	+21	16	0	5	7	+ 2	4	1	0	8	+19	12
0	1	2	+12	12	0	5	8	− 4	6	1	0	10	− 2	4
0	0	2	+34	26	0	5	9	+ 5	6	1	0	$\bar{2}$	−15	11
0	0	4	+22	16	0	6	1	+13	12	1	0	$\bar{4}$	+ 4	5
0	0	6	+32	26	0	6	2	+25	22	1	0	$\bar{6}$	+10	15
0	0	8	+15	12	0	6	3	+ 5	6	1	0	$\bar{8}$	+ 2	4
0	0	10	+17	12	0	6	4	+30	25	2	0	2	− 7	7
0	1	1	+37	33	0	6	6	+12	9	2	0	4	+14	12
0	1	2	+24	22	0	6	8	+ 9	8	2	0	6	+12	15
0	1	3	− 2	4	0	7	1	+14	12	2	0	8	− 2	4
0	1	4	+ 3	2	0	7	2	− 5	3	2	0	$\bar{2}$	+20	16
0	1	5	+18	19	0	7	3	+22	19	2	0	$\bar{4}$	−17	20
0	1	6	+ 5	4	0	7	5	+16	11	2	0	$\bar{8}$	+ 9	7
0	1	7	+ 8	10	0	7	6	+ 4	4	3	0	2	− 8	7
0	1	8	+ 5	6	0	7	7	+10	6	3	0	4	+ 7	9

TABLE II—(*Contd.*)

h	*k*	*l*	F_c	F_0	*h*	*k*	*l*	F_c	F_0	*h*	*k*	*l*	F_c	F_0
0	1	9	+ 9	6	0	7	8	− 2	4	3	0	6	+28	18
0	1	10	− 2	4	0	7	9	+ 7	6	3	0	8	+ 3	4
0	1	11	+ 3	4	0	8	1	+14	14	3	0	$\bar{2}$	+34	24
0	2	2	− 5	5	0	8	2	+24	19	3	0	$\bar{4}$	+11	11
0	2	3	−10	8	0	8	3	+ 3	2	3	0	$\bar{6}$	+ 8	8
0	2	4	+25	20	0	8	4	+11	9	3	0	$\bar{8}$	+16	11
0	2	5	+11	12	0	8	5	− 5	9	4	0	2	+ 4	5
0	2	6	+10	12	0	8	6	+11	8	4	0	4	+ 9	7
0	2	7	+ 4	2	0	8	8	+ 8	5	4	0	6	+15	8
0	2	8	+10	6	0	9	1	+ 4	8	4	0	8	+ 2	3
0	3	1	+17	15	0	9	2	+11	16	4	0	$\bar{2}$	+10	7
0	3	2	−34	34	0	9	3	+13	12	4	0	$\bar{4}$	+12	6
0	3	3	+ 3	5	0	9	5	+ 1	4	4	0	$\bar{6}$	+11	5
0	3	4	− 3	2	0	9	6	+ 6	8	4	0	$\bar{8}$	+ 8	8
0	3	5	+14	15	0	9	7	+ 6	7	5	0	2	− 3	5
0	3	6	+16	14	0	10	1	+ 1	4	5	0	4	+11	8
0	3	8	−12	10	0	10	2	+ 6	7	5	0	6	− 3	4
0	3	9	+ 8	7	0	10	5	+ 1	2	5	0	8	− 6	5
0	3	10	+ 7	8	0	11	1	+13	9	5	0	$\bar{2}$	+ 8	6
0	4	1	+ 9	6	0	11	2	− 8	10	5	0	$\bar{4}$	+ 6	6
0	4	2	+ 8	5	0	11	4	− 5	8	5	0	$\bar{6}$	− 6	5
0	4	3	−15	12	0	11	7	+ 5	6					
0	4	4	− 3	5	0	12	2	+ 9	11					

TABLE III

Bond lengths and angles

O_1–O_2	2·23 Å	Mg–O_1	2·11 Å
O_1–C_1	1·33	Mg–$H_2O_{(1)}$	2·08
O_2–C_1	1·25	Mg–$H_2O_{(2)}$	2·07
C_1–C_2	1·57		
O_1–C_1–O_2	120° 30′		
O_1–Mg–$H_2O_{(1)}$ ..	90° 48′		
$H_2O_{(1)}$–Mg–$H_2O_{(2)}$ ..	88° 48′		

4. CONCLUSIONS

The structure is anologous to that of nickel acetate. The two acetate groups are planar and are distributed with the magnesium atom at a centre of symmetry. Each magnesium atom is surrounded by four water molecules $H_2O_{(1)}$, $H_2O_{(2)}$, $\overline{H_2O}_{(1)}$, $\overline{H_2O}_{(2)}$, and oxygen atoms O_1 and O_1 (bars denoting the atoms belonging to other acetate group, not shown in the figure). The remaining oxygen atom $O_{(2)}$ is linked to $H_2O_{(2)}$. The acetate group belonging to the magnesium atom situated at $(0, \frac{1}{2}, \frac{1}{2})$ is also linked to the acetate group at (0, 0, 0) by hydrogen bond, as in the case of nickel acetate.

The bond distances between the magnesium atom and water molecules are 2·08 and 2·07 and the distance Mg – O, is 2·11 Å. These are in good agreement with the values obtained in the case of nickel acetate. The $O_1 - C_1$, and $O_2 - C_1$ are found to be 1·33 and 1·25, while in the case of nickel acetate they are reported to be nearly equal.

5. SUMMARY

The crystal structure of magnesium acetate has been completely determined. The crystals are monoclinic with space-group $C_{2h}^5 - P2_1/c$ and two molecules in a unit cell with edges $a = 4{\cdot}75$ Å, $b = 11{\cdot}79$ Å, $c = 8{\cdot}52$ Å and $\beta = 94° 54'$. The positions of the atoms were determined from electron density projections on the *bc* and *ac* planes. From these the various bond lengths and angles were calculated.

6. References

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