The Crystal Structure of Zinc Oxyacetate, $Zn_4O(CH_3COO)_6$

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Introduction

Zinc oxyacetate $Zn_4O(CH_3COO)_6$ has an analogous composition to beryllium oxyacetate $Be_4O(CH_3COO)_6$. Its stability, volatility[1] and, furthermore, its crystal structure reported in a study by Wyart[2] showed that it must be of the same type as $Be_4O(CH_3COO)_6$. However, the accurate shape and size of the molecule have not yet been reported. As an

1) N. V. Sidgwick: "Chemical Elements and their Compounds" p. 283, Oxford, (1950).

2) J. Wyart: *Bull. Soc. Franç. Min.*, **49**, 148 (1926).

extension of our work on beryllium oxyacetate[3,4], we have undertaken its complete structure determination.

Determination of the Structure

According to the method described by Auger and Robin[5] the compound was prepared by slowly distilling powdered anhydrous zinc acetate in a high vacuum. Zinc oxyacetate sublimed gradually and was collected as a crystalline crust on the cool place of the container. After being allowed to cool, the crystalline crust was examined and well-formed single crystals were picked out. They form small (up to 0.8 mm) transparent octahedra, which on prolonged exposure to moist air are hydrolysed and become opaque, while the corresponding beryllium compound is extremely stable. Crystals selected for the present study were octahedra of about 0.6 mm in each dimension and showed no remarkable cleavage.

Laue and complete sets of oscillation photographs were prepared. The latter were taken using Fe K_α radiation ($\lambda=1.937$ Å). The dimension of the unit cell, space group and other crystallographic data were found to be in good agreement with those obtained by the previous investigator[6]:

System: Cubic
Unit-cell dimension: $a=16.45$ Å ± 0.03 Å
Space group: O_h^7-Fd3m
Number of molecules per cell:
$Z=8$ units of $Zn_4O(CH_3COO)_6$
Density: $\rho_{obs.}=1.903$ g cm^{-3}.
$\rho_{calc.}=1.901$ g cm^{-3}.

The intensities of reflection were visually estimated with the aid of calibrated scales. The above-mentioned crystallographic data and general features of intensity of reflection indicated that the structure would be close to the cubic modification of beryllium oxyacetate. Referring to the structure of beryllium compound and making use of Patterson projection, atomic parameters were deduced and refined by the method of double Fourier series. Final atomic parameters are listed in Table I.

TABLE I

ATOMIC PARAMETERS

8	$O_{(1)}$	in 8(a)	000		
32	Zn	32(e)	xxx	with	$x=-0.069$
48	$C_{(1)}$	48(f)	$x00$		$x=0.220$
48	$C_{(2)}$	48(f)	$x00$		$x=0.314$
96	$O_{(2)}$	96(g)	xxz		$x=-0.047$
					$z=-0.185$

Structure amplitudes calculated and observed are given in Table II. The agreement was good and the value of $R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ is 0.18 for all (hkl) reflections. The temperature factor used is of the form $\exp -B(\sin\theta/\lambda)^2$, where $B=0.4$ Å^2.

3) T. Watanabe, Y. Saito and H. Koyama: *Nature*, **164**, 1046 (1949).
4) Y. Saito: X-rays, **7**, 9 (1952) (in Japanese).
5) V. Auger et I. Robin: *Compt. rend.* **178**, 1546 (1924).
6) J. Wyart: loc. cit.

TABLE II OBSERVED AND CALCULATED F-VALUE

hkl	$F_{obs.}$	$\|F_{calc.}\|$	hkl	$F_{obs.}$	$\|F_{calc.}\|$	hkl	$F_{obs.}$	$\|F_{calc.}\|$
111	19.8	24.4	1020	—	1.1	1244	—	2.3
220	7.4	9.3	862	9.5	8.7	1331	—	2.6
311	10.7	9.9	951	10.7	10.6	1175	4.5	4.0
222	18.7	21.9	773	8.7	8.0	1084	2.0	4.3
400	14.7	15.7	1022	11.4	12.9	1262	8.7	9.6
331	11.8	13.0	666	13.0	12.0	1333	10.1	10.8
422	11.3	10.0	953	10.3	10.9	995	1.5	2.2
511	10.9	11.0	864	3.0	5.7	1351	—	1.7
333	15.3	14.5	1042	4.2	4.2	1175	—	1.2
440	11.5	11.1	1111	1.4	3.5	1264	4.5	6.6
531	11.2	11.1	775	15.6	12.6	10100	7.9	6.1
442	19.0	20.5	880	31.1	27.4	1420	9.3	4.4
620	7.9	8.8	971	17.5	13.9	1086	4.0	3.3
533	10.9	9.6	1131	9.0	9.4	1191	2.2	3.5
622	15.4	13.9	955	9.4	8.1	1353	3.8	3.4
444	7.7	5.4	882	—	3.5	10102	11.1	11.7
551	2.1	1.7	1044	23.0	20.6	1422	3.8	5.4
711	15.0	16.6	1060	12.0	8.5	1280	2.3	2.0
642	5.8	4.8	866	16.7	15.0	1193	9.4	10.7
731	8.6	7.9	973	7.8	7.0	1282	1.6	0.8
553	14.0	11.7	1133	11.2	9.1	1442	—	2.2
800	27.7	32.7	1062	9.3	8.9	10104	—	1.6
733	6.3	4.6	1200	8.9	7.9	1371	6.9	7.5
644	10.2	10.0	884	—	1.4	1284	—	1.8
660	25.8	23.3	1151	7.4	9.3	1511	7.8	9.1

822	16.1	15.2	1222	2.8	4.8	1373	—	0.5
751	13.9	11.9	1064	—	1.0	1444	1.0	2.4
555	9.3	7.7	1153	11.6	14.5	1460	9.9	12.7
662	13.3	12.5	975	6.1	5.8	1531	3.5	4.3
840	3.5	4.6	1240	1.1	1.0	1462	2.6	4.9
911	12.4	11.8	991	11.8	11.0	1533	—	4.4
753	—	0.1	1242	13.6	12.3	11111	6.2	7.6
842	4.8	6.8	886	—	2.7	12102	4.9	6.1
664	—	0.2	1082	5.1	5.0	1464	2.2	3.6
931	2.7	3.7	1311	12.2	9.6	1551	6.2	8.2
844	—	0.8	1171	—	0.8	1391	3.0	3.3
771	14.2	14.4	993	9.5	9.0	11113	3.6	4.8
933	17.6	18.4	1155	9.1	9.8	1600	21.1	22.0
755	2.1	3.2	1066	4.7	6.0	1622	3.1	3.5

TABLE III

INTERATOMIC DISTANCES AND INTERBOND ANGLES

$Zn_4O(CH_3COO)_6$			$Be_4O(CH_3COO)_6$ (16°C)		
$O_{(1)}$	Zn	1.96 Å	$O_{(1)}$	Be	1.65 Å
$O_{(2)}$	Zn	1.98	$O_{(2)}$	Be	1.61
Zn	Zn	3.20	Be	Be	2.76
$C_{(2)}$	$C_{(1)}$	1.55	$C_{(2)}$	$C_{(1)}$	1.55
$C_{(2)}$	$O_{(2)}$	1.24	$C_{(2)}$	$O_{(2)}$	1.26
$O_{(2)}$	$O_{(2)}$	2.20	$O_{(2)}$	$O_{(2)}$	2.24
$O_{(2)}$	$O_{(2)}$	2.71	$O_{(2)}$	$O_{(2)}$	2.51
$\angle O_{(2)}C_{(2)}O_{(2)}$		125°	$\angle O_{(2)}C_{(2)}O_{(2)}$		126°

Description of the Structure

The interatomic distances and interbond angles calculated on the basis of the atomic parameters listed in Table 1 are given in Table III, together with those found in crystals of $Be_4O(CH_3COO)_6$.

The structure consists of $Zn_4O(CH_3COO)_6$ molecules having the shape shown in the Figure. The molecular symmetry is Td–$\bar{4}3m$, whereas that of $Be_4O(CH_3COO)_6$ is T–23. This difference in molecular symmetry arises from slightly different orientations of the acetate groups in the molecule. In $Zn_4O(CH_3COO)_6$ molecule, each acetate group lies on the plane containing central oxygen atom and one edge of Zn-tetrahedron, while in the case of the beryllium compound below the transition temperature (40°C) the planes containing OCO radicals are inclined at an angle of 12.7° with the planes of $O_{(1)}$ and one Be-Be edge. The Zn-O distances are in good agreement with those found in crystals of ZnO. In spite of the molecular nature of this compound, the size and shape of the acetate groups are, though not significant, in agreement with those found in other ionic structures.

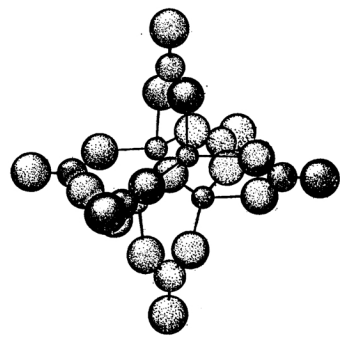

Fig. A molecule of zinc-oxyacetate

Summary

The crystal structure of $Zn_4O(CH_3COO)_6$ has been examined by the method of X-ray Fourier analysis (Fe $K\alpha$, $\lambda = 1.937$ Å). The general features of the structure reported by Wyart in 1926 are confirmed and the atomic co-oridinates which hitherto remained unfixed have been completely determined. Lengths of Zn-O bonds are 1.96 and 1.98 Å respectively, which are in good accord with those found in crystals of ZnO. The significance of the structure is discussed briefly and compared with that of $Be_4O(CH_3COO)_6$.

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