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Basic Beryllium Acetate: Part I. The Collection of Intensity Data*

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Two independent, three-dimensional sets of intensity data have been collected from two different crystals of basic beryllium acetate ($Be_4O(CH_3CO_2)_6$, cubic, $Fd3$, $a_0 = 15{\cdot}74$ Å, $Z = 8$). An Eulerian cradle Geiger counter spectrometer was employed for the measurements. Two crystals were surveyed so as to insure against systematic errors in the data. The integrated intensities of the two sets of data were obtained in different ways, one by stationary crystal-stationary counter and the other by moving crystal-moving counter. Each set of data is affected by a different kind of statistical counting error (constant count, fixed time count). The intensities of seven strong low order reflections that are affected by extinction in the data crystals have been determined from the consideration of two additional smaller crystals and a powder. The reproducibility of equivalent reflections has been tested in two different ways and has been found to be about 4% in intensity. A detailed comparison of the two sets of data has been carried out. The overall agreement, all reflections included, is of the order of 8% in intensity.

1. Introduction

The reinvestigation of the structure of basic beryllium acetate (hereinafter referred to as beryllium acetate) was undertaken to provide an absolute scattering scale for a series of isomorphous protein crystals. However, at an early stage in its refinement, some of the observed atomic electron-density distributions showed effects that could be attributed to chemical bonding and/or anharmonic thermal vibrations. In order to assure that such effects are real and not due to a systematic error or errors, a second set of three-dimensional intensity data was collected for analysis. The two sets of data were obtained from different crystals, the integrated intensities of the two sets were measured by different methods and a different kind of statistical counting error affects each set of data. The details of the analysis of this data are described in Parts II and III of this series of communications.

2. Experimental

(i) *General*

Crystals of beryllium acetate, $Be_4O(CH_3CO_2)_6$, were grown by Dr M. V. King of this laboratory. As small specimens were desired, they were prepared by rapid cooling of glacial acetic acid solutions of beryllium acetate. The crystals displayed octahedral morphology and two well-formed octahedra, 0·32 mm. on edge ($v \sim 1{\cdot}5 \times 10^{-2}$ mm.^{3}) and 0·15 mm. on edge ($v \sim 1{\cdot}6 \times 10^{-3}$ mm.^{3}), were chosen for the collection of independent sets of intensity data.

All the X-ray work (Cu $K\alpha$) was carried out in a constant temperature (21 °C.), air conditioned laboratory with an Eulerian cradle Geiger counter spectrometer (Furnas & Harker, 1955; Furnas, 1957). Preliminary measurements verified beryllium acetate to be cubic, space group $Fd3$, the mean cell edge of the two crystals being $15{\cdot}74 \pm 0{\cdot}01$ Å, with eight molecules in the unit cell (Bragg & Morgan, 1923; Morgan & Astbury, 1926). Since a general reflection in this space group is one of 24 equivalent reflections, the intensity surveys were confined to $\frac{1}{24}$th of the reciprocal sphere. This gives rise to 370 possible independent reflections within the range of the Eulerian cradle ($2\theta \leq 163{\cdot}5°$). The intensity data from the 0·32 mm. crystal were obtained using a stationary crystal-stationary counter technique; the data from the 0·15 mm. crystal were obtained using a moving crystal-moving counter (Cochran, 1950; Furnas, 1957).

(ii) *Stationary crystal-stationary counter data**

Diffraction maxima were first located with the aid of spherical coordinates computed from the fundamental lattice translation and peak positions were ascertained by varying spectrometer settings. A fixed slit-width (0·9°) Geiger counter was used in the recording of intensity measurements. For the 0·32 mm. crystal, the 0·9° width was found to be sufficient to contain a complete reflection out to $2\theta \sim 65°$. Beyond $2\theta \sim 65°$, both $K\alpha$ components could not be recorded completely. In this range, the $K\alpha_1$ component was measured, partially overlapped with $K\alpha_2$, and then corrected

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* Hereafter referred to as *SX*.

semi-empirically. Initially, a correction that was linear in the 2θ splitting range was used. However, in the latter stages of the structure analysis, the average value of the absolute scale constant as a function of $\langle 2\theta \rangle$ showed that this correction was inadequate. A new and more satisfactory one was deduced from these results. It is shown in Fig. 1 along with the initial linear correction.

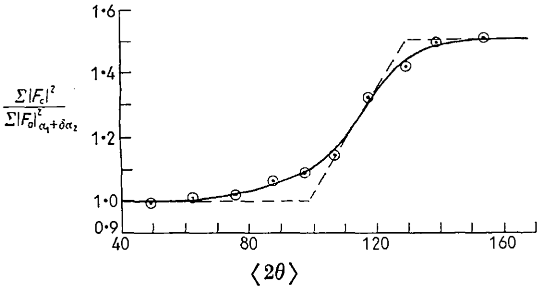

Fig. 1. $K\alpha$ splitting correction, solid—semi-empirically derived, broken—initial linear correction.

The 286 strongest reflections were measured by the time taken to record 1,024 counts and this was taken to be inversely proportional to the integrated intensity. Nickel filters (1, 3, 6, 9 and 12) were used with the very intense reflections to avoid counter coincidence errors. The filter scaling constants were obtained empirically and were known to 2–3%. The 84 weakest reflections were obtained from peak heights recorded on a logarithmic chart, the chart being calibrated against reflections of known intensity.

(iii) Moving crystal-moving counter data*

The counter moved at twice the angular velocity of the crystal. Each reflection was scanned in 2θ from background to background. Out to $2\theta \leq 140°$, a two degree scan was sufficient to contain both $K\alpha_1$ and $K\alpha_2$ components. At higher values of 2θ, the scanning angle was increased to three degrees. The mid-point of all the scans was $[2\theta(\alpha_1)+2\theta(\alpha_2)]/2$. Diffraction maxima were again located from precomputed spherical coordinates.

Intensities were obtained using a balanced Ni–Co filter pair. Reflections were scanned with the Ni filter followed by an identical scan with the Co filter. The difference in counts, empirically corrected for the balanced filter window width, was taken to be proportional to the integrated intensity. The window width correction was obtained by taking the difference in counts between Ni and Co filter scans offset two degrees in 2θ and one degree in azimuthal orientation from $(h/2, h/2, h/2)$ positions ($h=1, 5, 9, \ldots, 25$).

Two scanning rates were employed so as to improve the reliability of the weaker reflections. When the statistical relative fluctuation of an intensity approached 15% on a fast scan (2°/min.), a slow scan was taken (2°/10 min.). In all, 160 reflections were fast scanned. Nickel filters (3 and 6) were again used to reduce the stronger intensities. The number of nickel filters required by a given reflection was determined by measuring the number of counts per 10 sec. of the $K\alpha_1$ component of the reflection by the *SX* technique. Of all the reflections, it was impossible to obtain the $K\alpha_2$ component of (14, 14, 4) and (20, 2, 2). In these two cases, the $K\alpha_1$ component was measured with a two degree scan and multiplied by 1·5.

(iv) *Extinction and absorption*

After several cycles of refinement, and therefore structure factor computation, it became apparent that some of the strong low order reflections were seriously affected by extinction. In an effort to obtain more reliable intensities for such reflections, two smaller crystals (0·03 and 0·06 mm. on edge) and a powder were examined. Comparison of all the available data showed that extinction in the data crystals was confined to $2\theta \leq 36{\cdot}1°$. Of the 15 reflections in this range, eight are weak enough not to show extinction effects.

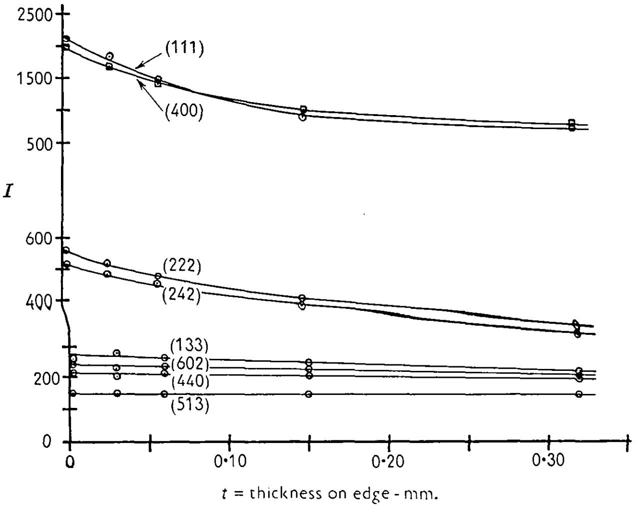

Fig. 2. Extinction affected reflections as a function of crystal size, (513) included for comparison, intensity in arbitrary units, powder point near $t=0$.

Fig. 2 shows how the seven extinction affected reflections behave as a function of crystal size. The (513) reflection is included for comparison. From the behavior of the extinction affected reflections, it will be seen that they have a primary extinction contribution. Extrapolated values of these intensities were used for both sets of data in the structure analysis.

The linear absorption coefficient for beryllium acetate is 11·5 cm.$^{-1}$ so that the 0·32 mm. crystal absorbs about 30% and the 0·15 mm. crystal about 16% of its scattered radiation. However, as the maximum change in absorption with diffraction angle is only of the order of 2% for the larger crystal, the intensities from the two crystals were not corrected for absorption.

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* Hereafter referred to as *MX*.

(v) *Equivalent reflections*

The reproducibility of the intensities of equivalent reflections was investigated in two different ways. All the equivalent reflections of the (20, 0, 0), six, the (10, 6, 0), twelve, the (888), eight, and the (12, 2, 6), twenty four, were measured by the MX technique. The observed standard deviation from the mean intensity of these reflections was found to be about 4% in intensity. The intensity of 56 reflections, chosen at random with intensities varying over a wide range, was measured twice, (hkl) and (lhk), by the SX technique. The agreement in this set was assessed by evaluating

$$2\Sigma|I(hkl)-I(lhk)|/\Sigma[I(hkl)+I(lhk)]\ .$$

This was found to be 0·047.

The better agreement in the MX experiments can be attributed to the moderately strong intensities of the reflections chosen for this group. This gave better overall counting statistics. However, the observed standard deviations in this group are greater than counting statistics. Therefore, if all reflections were measured to a precision comparable to the foregoing, the best physically meaningful structure that could possibly be derived for beryllium acetate would have to have an R-factor,

$$R\sim 0{\cdot}02-0{\cdot}025,\ R=\Sigma||F_o|-|F_c||/\Sigma|F_o|\ .$$

(vi) *Comparison of the two sets of data*

The overall agreement between the two sets of data, all reflections included, has been approximated as

$$\Sigma||F_o|_{MX}-|F_o|_{SX}|/\Sigma|F_o|_{MX}\ ,$$

where $|F_o|_{MX}$ is the MX data, $|F_o|_{SX}$ the SX data and $\Sigma|F_o|_{MX}=\Sigma|F_o|_{SX}$. This was found to be 0·041.

A detailed comparison of the two sets of data was carried out by approximating to each observed structure amplitude, its standard deviation (*sd*), $\sigma(|F_o|)$. The approximation made was based upon counting statistics and known uncertainties introduced into the data. These were assumed to be independent of one another.

The $\sigma(|F_o|_{MX})$'s were taken to be a function of $\sigma(I)$ and $\sigma(k_{\rm Ni})$, where $\sigma(I)$ is the *sd* of the intensity measurement, $\sigma(I)=(I+2B)^{\frac{1}{2}}$, B being the background count and $\sigma(k_{\rm Ni})$ is the *sd* of the nickel filter scaling constant. The $\sigma(|F_o|_{SX})$'s were more complex. They included: counting statistics ($\sigma(I)=(1024)^{\frac{1}{2}}$ for the constant count reflections, $\sigma(I)=$ constant for logarithmically recorded reflections), $\sigma(k_{\rm Ni})$, the *sd* of the $K\alpha$ splitting correction and the *sd* of the scaling constant for the chart recorded intensities.

The quantities

$$\Sigma\sigma(|F_o|_{MX})/\Sigma|F_o|_{MX}\ \text{ and }\ \Sigma\sigma(|F_o|_{SX})/\Sigma|F_o|_{SX}\ ,$$

all reflections included, were evaluated and found to be 0·036 and 0·032, respectively. They are shown in Fig. 3 as a function of $\sin\langle\theta\rangle$. The maximum and minimum in the SX data can be attributed to the onset and completion of the $K\alpha$ splitting correction. The form of the MX data is due to the mode of approximating $\sigma(I)$. If it is assumed that $I\gg 2B$, or alternatively, that background counting is negligible ($B=0$), and that random errors in $|F_o|$'s are only due to counting statistics, it can be shown that

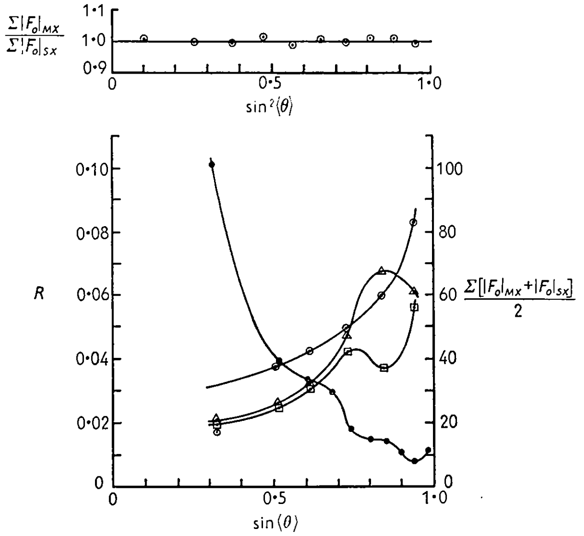

Fig. 3. Comparison of the SX and MX data, solid circles $-\Sigma[|F_o|_{MX}+|F_o|_{SX}]/2$ in electrons per cell, circles $-\Sigma||F_o|_{MX}-|F_o|_{SX}|/\Sigma|F_o|_{MX}$ where $\Sigma|F_o|_{MX}=\Sigma|F_o|_{SX}$, triangles $-\Sigma\sigma(|F_o|_{MX})/\Sigma|F_o|_{MX}$, squares

$$-\Sigma\sigma(|F_o|_{SX})/\Sigma|F_o|_{SX}\ ,$$

all versus constant shells.

$$\sigma^2(|F_o|)=k\Phi/4\ ,$$

where k is the absolute scale constant of the intensities and Φ is the Lorentz and polarization factor. In the present case, $\Phi=\sin 2\theta/(1+\cos^2 2\theta)$ and since the fall off of the observed data approximates Wilson behavior (Fig. 3), a maximum occurs in the vicinity of $\sin\theta=0{\cdot}85$. Deviations from ideal behavior of $\Sigma\sigma(|F_o|_{MX})/\Sigma|F_o|_{MX}$ occur in the low orders (maximum difference $\sim 0{\cdot}015$) and very high orders (maximum difference $\sim 0{\cdot}006$). This can be attributed to the collapse of the original assumptions: in the low orders, transmission through the Co filter was appreciable and nickel filter scaling errors were involved; in the high orders, a large proportion of the data was of weak intensity, not very much greater than background. The first point in the SX–MX comparison is erratic because the same values for the extinction affected reflections were used in both sets of data.

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Basic Beryllium Acetate: Part II. The Structure Analysis*

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A detailed structure analysis, employing three-dimensional Fourier methods, has been carried out on beryllium acetate. Two sets of independent intensity data were used for this purpose. The observed structure has been approximated through positional parameters, individual and general harmonic thermal vibrations and electron count parameters. The last two were fixed from difference density considerations in non-bonding directions. The final calculated structure agrees well with the observed structures except in certain regions of the acetate groups: there are effects present in the C–C and C–O bonds which suggest chemical bonding and/or anharmonic thermal vibrations; the acetate groups appear to possess a rigid body type angular oscillation about their C–C bonds. Half-weight hydrogen atoms of orientationally disordered methyl groups (two equally probable equilibrium orientations) have been located.

1. Structure analysis

(i) *General atomic arrangement*

The point group symmetry of a molecule of beryllium acetate is 23 and symmetry requirements fix all but six positional parameters in the asymmetric unit, hydrogen atoms excluded.

Within a molecule, there is a central oxygen atom, O_I, and it is located at the intersection of three 2-fold rotation axes. Choosing this point as an origin, beryllium atoms surround it on 3-fold rotation axes at $\bar{u}uu$, $u\bar{u}u$, $uu\bar{u}$ and $\bar{u}\bar{u}\bar{u}$. The six acetate groups are arranged octahedrally about the origin, the carbon atoms lying on the 2-fold axes, the carboxyl carbon, C_I, at v, the methyl carbon, C_{II}, at w. As the acetate groups possess 2-fold symmetry, the carboxyl oxygen atoms, O_{II}, are equivalent. However, their positions are general. The hydrogen atoms of the methyl groups are also in general positions and if the space group is truly *Fd*3, their arrangement must satisfy 2-fold symmetry.§ Since methyl groups do not possess such a symmetry, it becomes clear that they must be orientationally disordered.

Chemical considerations require the carboxyl groups

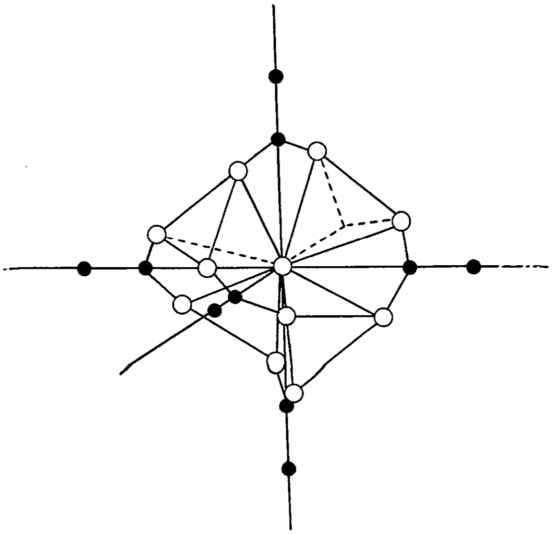

Fig. 1. Atomic arrangement in one molecule, shaded-carbon, circles-oxygen, Be (not shown) near centers of oxygen tetrahedra, one acetate missing.

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§ That the space group is, in fact, *Fd*3 is borne out by the fact that the intensities of reflections of the type *hkl* have been shown to be equivalent to a high degree throughout reciprocal space (Part I).