interactions to occur in the molecule of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II).

The significant differences in the two copper–oxygen bond lengths [Cu(1)–O(3), 1·90; Cu(1)–O(4), 2·00 Å] and the two carbon–oxygen bond lengths [C(5)–O(3), 1·36; C(1)–O(4), 1·27 Å] indicate that the presence of the fused benzene ring has largely destroyed any resonance system in the chelate ring, of the type found in some metal complexes with β-diketones, such as the acetylacetonato complexes (Calvin & Wilson, 1945).

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# The Wurtzite *Z* Parameter for Beryllium Oxide and Zinc Oxide


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The *z* parameter in BeO and ZnO has been determined by single-crystal neutron diffraction measurements. For BeO, $z = 0{\cdot}3786 \pm 0{\cdot}0015$, and for ZnO, $z = 0{\cdot}3826 \pm 0{\cdot}0007$.


## Introduction

BeO and ZnO crystallize in the polar space group $P6_3mc$ and have the wurtzite structure. There are two atoms of each kind in the unit cell and these are assigned to the special positions 2(*b*) so that metal atoms occupy the sites $\frac{1}{3},\frac{2}{3},0$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ while the oxygen atoms are at $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}+z$. There is only one structural parameter *z* and several attempts have been made to measure it because of its relevance to bonding calculations.

## Structure analysis

(1) BeO

Jeffrey, Parry & Mozzi (1956) and later Smith, Newkirk & Kahn (1963) used single-crystal X-ray methods and obtained $z = 0{\cdot}378$ and $0{\cdot}3786 \pm 0{\cdot}0005$ respectively Pryor & Sabine (1964) found a result of $0{\cdot}3778 \pm 0{\cdot}001$

by neutron powder methods while Sabine & Dawson (1963) obtained $0{\cdot}374 \pm 0{\cdot}002$ from X-ray powder patterns.

There are two difficulties in determining the $z$ parameter in BeO with X-rays. The first is the very high perfection of BeO crystals leading to severe extinction effects which are difficult to allow for in analysing the data; the second is the lack of knowledge of the valency state of the atoms and hence the X-ray scattering factors. Sabine & Dawson found that the choice of these had a marked effect on the atomic parameters derived from the analysis.

To overcome the first problem, a crystal which Austerman (private communication) had found to be unusually imperfect was used. The second difficulty was overcome by the use of neutron diffraction.

*Experimental*

The crystal, of mass 12·8 mg, was roughly in the form of a squat cone with **c** along the cone axis. The lattice parameters were taken as $a=2{\cdot}6984$, $c=4{\cdot}2770$ Å (Hickman, Sabine & Coyle, 1962). It was mounted on a four-circle diffractometer on the reactor HIFAR and the intensities of all reflexions with $\sin\theta/\lambda < 0{\cdot}7$ measured. The neutron beam intensity was $4\times10^6$ ncm$^{-2}$ sec$^{-1}$ at a wavelength of 1·09 Å.

Table 1. *The magnitudes of the observed and calculated structure factors for beryllium oxide* ($\times 100$)

| $h$ | $k$ | $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|
| 0 | 0 | 2 | 189 | 195 |
| 0 | 0 | 4 | 47 | 45 |
| 0 | 0 | 6 | 149 | 154 |
| 1 | 0 | 0 | 131 | 134 |
| 2 | 0 | 0 | 133 | 127 |
| 3 | 0 | 0 | 222 | 233 |
| 1 | 0 | 1 | 92 | 92 |
| 1 | 0 | 2 | 99 | 96 |
| 1 | 0 | 3 | 193 | 202 |
| 1 | 0 | 4 | 26 | 23 |
| 1 | 0 | 5 | 191 | 194 |
| 1 | 0 | 6 | 81 | 76 |
| 2 | 0 | 1 | 88 | 88 |
| 2 | 0 | 2 | 102 | 91 |
| 2 | 0 | 3 | 188 | 192 |
| 2 | 0 | 4 | 19 | 24 |
| 3 | 0 | 2 | 160 | 168 |
| 1 | 1 | 0 | 251 | 258 |
| 1 | 1 | 2 | 181 | 185 |
| 1 | 1 | 4 | 46 | 47 |
| 2 | 1 | 0 | 120 | 121 |
| 2 | 1 | 1 | 87 | 86 |
| 2 | 1 | 2 | 88 | 87 |
| 2 | 1 | 3 | 191 | 183 |

The data were refined by the *ORFLS* program (Busing, Martin & Levy, 1962) with standard deviations allotted to the observed intensities through the expression $\sigma=\sigma_1+\sigma_2$ where $\sigma_1$ is the standard deviation resulting from counting statistics alone (which in this case was negligible) and $\sigma_2=\alpha+\beta P$ where $P$ is the observed intensity and $\alpha$ and $\beta$ are constants chosen by repeated measurements on several symmetry-related reflexions to be 150 and 0·04.

The least-squares refinement was based on $F$, and the parameters varied were $z$, the overall scale factor and an isotropic temperature factor for each atom. An attempt was made to use anisotropic temperature factors; however, the correlation between the variables was so high that the parameters were physically meaningless. The refinement converged to an $R$ value of 0·036.

Observed and calculated structure factors are given in Table 1, and positional and thermal parameters in Table 3.

Table 2. *The magnitudes of the observed and calculated structure factors for zinc oxide* ($\times 100$)

| $h$ | $k$ | $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|
| 0 | 0 | 2 | 168 | 171 |
| 0 | 0 | 4 | 235 | 217 |
| 0 | 0 | 6 | 120 | 124 |
| 1 | 0 | 0 | 111 | 116 |
| 1 | 0 | 1 | 77 | 72 |
| 1 | 0 | 2 | 88 | 84 |
| 1 | 0 | 3 | 180 | 174 |
| 1 | 0 | 4 | 12 | 11 |
| 1 | 0 | 5 | 172 | 177 |
| 1 | 0 | 6 | 65 | 62 |
| 1 | 1 | 0 | 215 | 226 |
| 1 | 3 | 0 | 105 | 101 |
| 1 | 3 | 1 | 66 | 63 |
| 1 | 3 | 2 | 75 | 74 |
| 1 | 3 | 3 | 149 | 151 |
| 2 | 0 | 0 | 116 | 112 |
| 2 | 0 | 1 | 77 | 70 |
| 2 | 0 | 2 | 87 | 82 |
| 2 | 0 | 3 | 171 | 168 |
| 2 | 0 | 4 | 8 | 11 |
| 2 | 0 | 5 | 166 | 171 |
| 2 | 0 | 6 | 62 | 59 |
| 2 | 1 | 0 | 111 | 108 |
| 2 | 1 | 1 | 72 | 67 |
| 2 | 1 | 2 | 83 | 79 |
| 2 | 1 | 3 | 160 | 162 |
| 2 | 1 | 4 | 6 | 11 |
| 2 | 1 | 5 | 159 | 165 |
| 2 | 2 | 0 | 199 | 204 |
| 2 | 2 | 2 | 150 | 149 |
| 3 | 0 | 0 | 203 | 211 |
| 3 | 0 | 2 | 151 | 154 |
| 3 | 0 | 4 | 21 | 22 |

Table 3. *Atomic and thermal parameters with their estimated standard deviations*

Thermal parameters are in the form $\exp[-(B\sin^2\theta/\lambda^2)]$.

| | $z$ | $\sigma(z)$ | $B_O$ | $\sigma(B_O)$ | $B_M$* | $\sigma(B_M)$ |
|---|---|---|---|---|---|---|
| BeO | 0·3786 | 0·0015 | 0·53 Å$^2$ | 0·09 Å$^2$ | 0·27 Å$^2$ | 0·08 Å$^2$ |
| ZnO | 0·3826 | 0·0007 | 0·55 | 0·08 | 0·31 | 0·06 |

* M = metal ion.

(2) ZnO

An X-ray determination of the $z$ parameter in ZnO has been made by Harrison, Jeffrey & Townsend (1958) who found that the necessity to correct the zinc scattering factor for anomalous dispersion prevented them from obtaining an accurate value.

A neutron powder study by Nitts, Papulova, Sosnovskaya & Sosnovskij (1964) gave a value of 0·374. The initial object of the present work was an accurate determination of $z$ from single-crystal neutron data. However, after the work was complete an X-ray determination by Abrahams & Bernstein (1969) came to our attention in which they obtained $z=0{\cdot}3825\pm 0{\cdot}0014$.

The crystal was supplied by Semi-Elements and was a rough cube of 16·95 mg. The lattice parameters were taken as $a=3{\cdot}2427$, $c=5{\cdot}1948$ Å (Hickman, private communication). The intensity data were collected in an identical way to the BeO data and the analysis carried out in the same way.

As with BeO the use of anisotropic temperature factors gave meaningless results; the refinement based on isotropic temperature factors converged to $R=0{\cdot}047$.

The observed and calculated structure factors are shown in Table 2 and the positional and thermal parameters in Table 3. Table 4 gives the correlation matrices for BeO and ZnO.

Table 4. *Correlation matrices in least squares analysis*

| | Overall scale factor | $B_M$ | $z$ | $B_O$ |
|---|---|---|---|---|
| BeO | 1·000 | 0·885 Å² | −0·232 | 0·725 Å² |
| | | 1·000 | −0·224 | 0·776 |
| | | | 1·000 | −0·497 |
| | | | | 1·000 |
| ZnO | 1·000 | 0·664 | −0·145 | 0·618 |
| | | 1·000 | 0·207 | 0·109 |
| | | | 1·000 | −0·521 |
| | | | | 1·000 |

## Discussion

(1) Jeffrey suggested that the deviation of the $z$ parameter, $\Delta z$, from its ideal value of 0·375, is related to the deviation of the $c/a$ ratio from 8/3 by the expression

$$\Delta z=\tfrac{2}{3}(a/c)^2-\tfrac{1}{4}\,.$$

This expression gives $z$ as 0·3786 and 0·3843 for BeO and ZnO respectively. The result of $0{\cdot}3786\pm 0{\cdot}0005$ obtained by Smith *et al.* (1963) and the present value of $0{\cdot}3786\pm 0{\cdot}0015$ support the use of this expression for BeO; however, the present values of $0{\cdot}3826\pm 0{\cdot}0007$ and the result of $0{\cdot}3825\pm 0{\cdot}0014$ (Abrahams & Bernstein, 1969) show that it does not predict the correct deviation from the ideal value of 0·375 for ZnO. The $z$ parameter in ZnO is further away from the ideal value than that for BeO and is hence a more sensitive test of the formula.

(2) The thermal vibration parameters found by various sets of authors for BeO are given in Table 5. The agreement between the present work and the X-ray work of Sabine & Dawson is probably fortuitous and the set that is more likely to be correct is that of Pryor & Sabine.

For ZnO, Abrahams & Bernstein find $B_O=0{\cdot}63$ and $B_{Zn}=0{\cdot}68$ while in the present work these parameters are 0·55 and 0·31 respectively.

It has been noticed that the errors resulting from extinction tend to accumulate on one of the thermal parameters in a structure analysis of simple compounds and this, together with the fact that the temperature factors for both atoms would be expected to be very nearly equal, suggests that a small amount of extinction in the ZnO data is the reason for this discrepancy. Abrahams & Bernstein (1969) applied an extinction correction and their values are probably more physically meaningful.

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Table 5. *Thermal parameters for* BeO (Å²)

| | Jeffrey *et al.* (1) | Jeffrey *et al.* (2) | Smith *et al.* (3) | Pryor & Sabine (4) | Sabine & Dawson (5) | Present work (6) |
|---|---|---|---|---|---|---|
| $B_{BE}$ | 0·60 | 0·53 | 0·48 | 0·35 ± 0·06 | 0·23 ± 0·18 | 0·27 ± 0·08 |
| $B_O$ | 0·27 | 0·20 | 0·61 | 0·27 ± 0·05 | 0·63 ± 0·14 | 0·53 ± 0·09 |

(1) X-ray, powder; (2) X-ray, single crystal; (3) X-ray, single crystal; (4) Neutron, powder; (5) X-ray, powder; (6) Neutron, single crystal.