

## On the Crystal Structure of a Lead(II) Bromide Hydrate, $3\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$

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The crystal structure of a compound with the stoichiometric formula  $3\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$  has been investigated, and preliminary results are presented in this communication.

Crystals of the compound were prepared by dissolving commercially available lead(II) bromide (BDH) in water and evaporating the solution. The translucent, needle-like crystals were analyzed by DTA methods using a Mettler Recording Thermoanalyzer, and were found to have the formula  $3\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$ . They are unstable in air and rapidly lose water, becoming opaque.

For the X-ray investigation, crystals cut to a suitable size were mounted in capillaries. The layers  $h0l-h3l$  and  $hk0-hk1$  were registered with  $\text{CuK}\alpha$  radiation using multiple film Weissenberg techniques. Since the compound disintegrated in the X-ray beam, a new crystal was used to register each layer.

The crystals were found to be monoclinic with the following cell dimensions:

$$a = 12.246 \text{ \AA}, b = 4.327 \text{ \AA}, c = 12.477 \text{ \AA}, \\ \beta = 101.37^\circ, V = 648.2 \text{ \AA}^3.$$

The density of the compound, as determined by the loss of weight in benzene, was found to be  $5.84 \text{ g cm}^{-3}$ , indicating that there are two formula units of  $3\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$  in the unit cell.

The only systematically absent reflections are  $0k0$  for  $k=2n+1$ , suggesting the space group to be either No. 4,  $P2_1$  or No. 11,  $P2_1/m$ .<sup>1</sup>

From the X-ray films it could be seen that the intensities of the  $h0l$  reflections were very similar to those of the  $h2l$  reflections with the same  $h$  and  $l$  values, the corresponding relation also being true for the  $h1l$  reflections and the  $h3l$  reflections. This information and the fact that the  $b$  axis is only  $4.32 \text{ \AA}$  makes it probable that the unit cell contains two layers of atoms perpendicular to the  $b$  axis.

A three-dimensional Patterson synthesis was calculated from  $Lp$ -corrected  $h0l$  and  $h1l$  Weissenberg data. Assuming the lead and bromine atoms to be situated in the point position  $P2_1/m: 2(e)$ ,<sup>1</sup> it was possible to determine the  $x$  and  $z$  parameters of all these atoms in the unit cell. After the lead and bromine positions had been refined, a three-dimensional difference electron density map yielded the positions of the four oxygen atoms. A least squares refinement including the lead, bromine, and oxygen atom positions gave an  $R$ -value of 15.4 %.

The structure is to be refined further using additional Weissenberg data and the intensities of the reflections will be corrected for absorption errors.

Fig. 1 shows a projection of the structure on the  $xz$  plane. Each lead atom is surrounded by eight other atoms, six of which

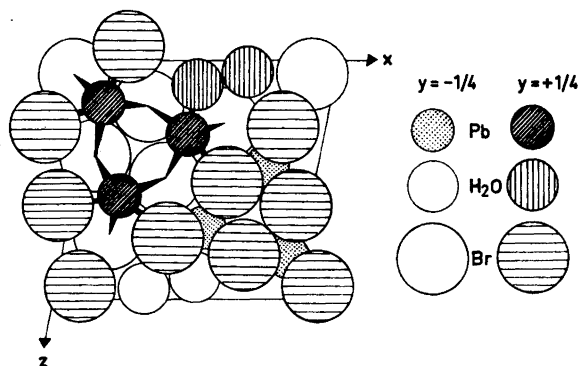


Fig. 1. A projection of the structure of  $3\text{PbBr}_2 \cdot 2\text{H}_2\text{O}$  on the  $xz$  plane.

lie at the apices of a trigonal prism and the remaining two beyond the centres of two of the three prism faces. This corresponds to a 9-coordination with one of the coordination sites unoccupied. The Pb—Br distances range from 2.94 Å to 3.47 Å, the mean value being 3.20 Å. The Pb—O bond distance is 2.59 Å.

A full report of the structure determination will soon be published in this journal.

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1. *The International Tables for X-ray Crystallography*, 2nd. Ed., Kynoch Press, Birmingham 1952, Vol. I.

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### Synthesis of 2,4- and 3,6-Di-*O*-methyl-D-mannose

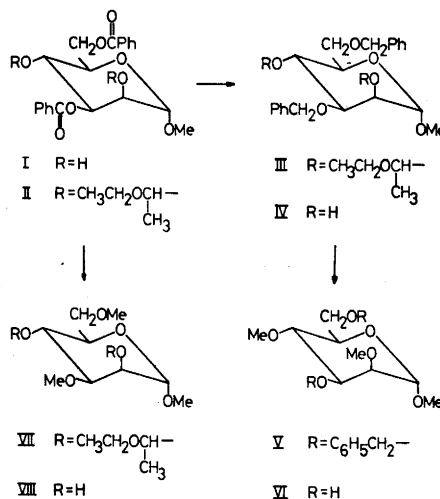
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Methyl 3,6-di-*O*-benzoyl- $\alpha$ -D-mannopyranoside is readily prepared by partial benzoylation of methyl  $\alpha$ -D-mannopyranoside<sup>1</sup> and should provide a convenient starting material for the syntheses of 2,4- and 3,6-di-*O*-methyl-D-mannose. These substances, which were needed in connection with methylation analysis of polysaccharides, containing D-mannose residues, had not previously been synthesized at the outset of the present work. Recently, however, Bhattacharjee and Gorin<sup>2</sup> reported the synthesis of the pure 2,4-dimethyl ether and of the 3,6-isomer, contaminated with other ethers. Another synthesis of the 2,4-dimethyl ether was reported by Murty and Siddiqui<sup>3</sup> and methyl 3,6-di-*O*-methyl- $\alpha$ -D-mannopyranoside was obtained, by Handa and Montgomery,<sup>4</sup> as one of several products on

partial methylation of methyl  $\alpha$ -D-mannopyranoside.

Methyl 3,6-di-*O*-benzoyl- $\alpha$ -D-mannopyranoside (I) was converted, by treatment with ethyl vinyl ether and an acidic catalyst, into the 2,4-di-*O*-(1'-ethoxyethyl) derivative (II) which provided the starting material for both syntheses. Syrupy II (a mixture of stereoisomers) was debenzoylated and then benzylated to give III. Removal of the 1'-ethoxyethyl groups by mild acid hydrolysis yielded IV, which upon methylation and subsequent removal of the benzyl groups by catalytical hydrogenation of the intermediate V, gave methyl 2,4-di-*O*-methyl- $\alpha$ -D-mannopyranoside, VI. Acid hydrolysis of VI yielded the crystalline 2,4-di-*O*-methyl-D-mannose. The total yield from I was 26 %.



Methyl 3,6-di-*O*-benzoyl-2,4-di-*O*-(1'-ethoxyethyl)- $\alpha$ -D-mannopyranoside (II) on debenzoylation and subsequent methylation yielded VII. This on mild acid hydrolysis yielded methyl 3,6-di-*O*-methyl- $\alpha$ -D-mannopyranoside, VIII, in a total yield from I of 50 %. Part of the amorphous VIII was converted into the crystalline 2,4-di-*O*-*p*-nitrobenzoate. 3,6-Di-*O*-methyl-D-mannose was prepared by acid hydrolysis of VIII.

The syntheses were followed by TLC and most of the products characterized by NMR. The structures of the 2,4- and 3,6-di-*O*-methyl-D-mannose were confirmed by converting them into the alditol ace-