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THE CRYSTAL STRUCTURE OF LEAD(II) IODIDE-DIMETHYLSULPHOXIDE(1/2), $PbI_2(dmso)_2$

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The crystal structure of the title compound has been determined by X-ray diffractometry. Two dimethylsulphoxide molecules co-ordinate to the Pb atom through their O atoms in trans position. The skeletal structure is a linear chain of $[>Pb<^{I}_{I}>]$ unit.

Though intercalation by PbI_2 crystals has been reported recently[1,2], no crystal structure of the intercalated compounds has yet been clarified. The title compound was subjected to crystal structure analysis in order to reveal the details of the intercalation. However the compound is an addition compound.

We attempted to grow single crystals of intercalated PbI_2 by the immersion of PbI_2 single crystals in dimethylsulphoxide(dmso) solution. The crystals, however, dissociated into powders(A), loosing their specific yellow colour. On the other hand, from saturated solution of dmso with PbI_2, colourless transparent needle crystals were obtained(B). Both A and B show the identical X-ray powder diffraction patterns, indicating that they are the same compound. The reaction of PbI_2 with dmso is reversible; A and B recover original yellow colour in air, indicating the removal of dmso molecules from PbI_2.

The oscillation photograph around the c axis shows super structure lines which were ignored in the present study. The crystals are orthorhombic with space group C222, Cmm2 or Cmmm, a=11.077(4), b=13.837(4), c=4.516(2) Å, μ(Mo Kα, λ=0.7107 Å)=167.5 cm^{-1}, D_x=2.96, D_m=2.84 g cm^{-3} and Z=2.

Intensity data were collected on a Rigaku automated four-circle diffractometer up to 2θ=60° with graphite monochromated Mo Kα radiation, using a crystal of dimensions ca. 0.2×0.2×0.5 mm. Absorption correction was made assuming cylindrical crystal shape.

The structure was solved by the heavy-atom method assuming space group Cmmm. The positional and anisotropic thermal parameters for non-hydrogen atoms were refined by the block-diagonal least-squares method. Calculations were carried out on a FACOM 230-38s of this University. The final R value for 481 independent reflexions is 0.119. A perspective drawing of the crystal structure is illustrated in Fig. 1. Bond distances and angles are listed in Table 1.

The crystal has skeletal linear chain structure consisting of $[>Pb<^{I}_{I}>]_n$. Although there is a disorder about the position of the dmso molecules, two dmso molecules co-ordinate to the Pb atom through their O atoms in trans position. The dmso molecules exhibit rotational and enantiomeric disorder around the Pb-O bond,

thus the S and C(2) atoms could not be located. The Pb-I bond distance [3.235(3) Å] is similar to that observed in the normal PbI_2 crystal, the Pb-I-Pb bond angle [88.5(1)°] agrees with that in the PbI_2. Accordingly the periodical structure of the >Pb<$\frac{I}{I}$>Pb< along the chain corresponding to the a axis in the 2H structure of the PbI_2 retains in this crystal. This indicates that the chain structure is derived from the layered structure of the PbI_2. The Pb-O bond distance of 2.38(6) Å is in accord with Pb-O single bond distance[3]. Therefore the resulting structure may be regarded as an addition compound of PbI_2 and dmso.

The reason why the PbI_2 crystal dissociate into powders on absorbing dmso could be interpreted as follows: when the dmso co-ordinates to the Pb atom of the PbI_2, direction of the Pb-O bond formation is indeterminate. Thus the linear chain structure could not be retained and the crystals dissociate into powders.

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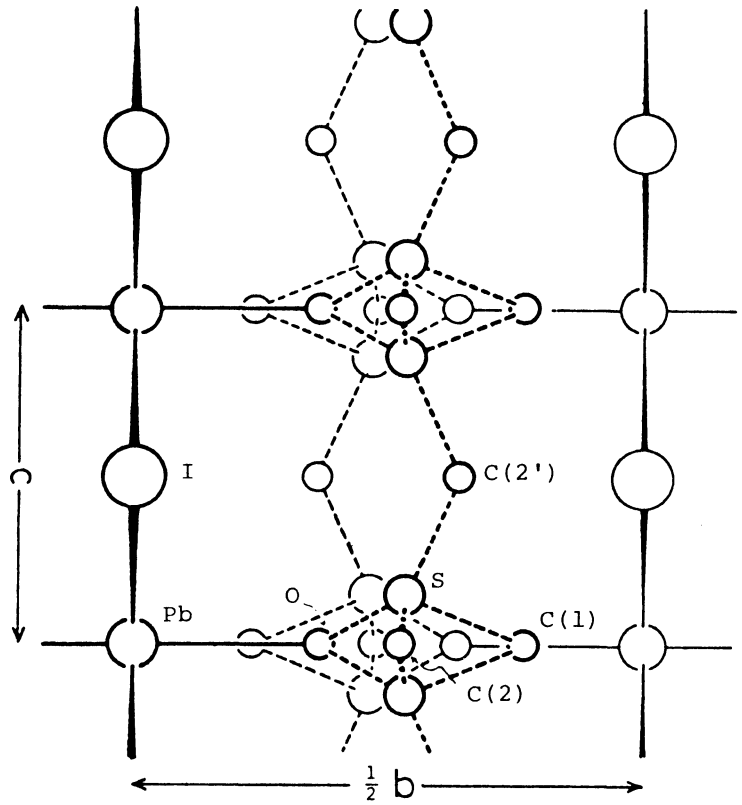

Fig. 1. Partial projection of the structure along the a axis

Table 1. Bond distances (Å) and angles (°)

Pb—I	3.235(3)
Pb—O	2.38(6)
S—O	1.48(6)
S—C(1)	1.77(9)
S—C(2)	1.69(12)
S—C(2')	1.88(24)
Pb—I—Pb'	88.5(1)
Pb—O—S	143(3)
O—S—C(1)	114(4)
O—S—C(2)	107(5)
O—S—C(2')	127(8)
C(1)–S—C(2)	111(5)
C(1)–S—C(2')	86(8)

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