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Preliminary communication

The structures of trimethylarsenic dichloride and dibromide

M.B. HURSTHOUSE and I.A. STEER*

Department of Chemistry, Queen Mary College, Mile End Road, London, E.1 (Great Britain)

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Spectroscopic studies[1,2] led to the suggestion that trimethylarsenic dichloride and dibromide had different structures, with the molecular dichloride possessing a trigonal bipyramidal configuration and the dibromide having an ionic structure $[Me_3AsBr]^+Br^-$. We have now confirmed this by single crystal X-ray analysis.

Both dihalides were prepared by adding a carbon tetrachloride solution of the appropriate halogen to an etherial solution of trimethylarsine. Crystals of the dichloride were obtained by sublimation and the dibromide by recrystallisation from acetonitrile. Crystal data: (*i*) $(CH_3)_3AsCl_2$; *m* 190.92. Hexagonal, *a* 7.05, *c* 8.23 Å, d_m 1.78, *Z* 2, d_c 1.79, spacegroup $P6_3/mmc$; (*ii*) $(CH_3)_3$ $AsBr_2$; *m* 279.83. Hexagonal, *a* 7.12, *c* 9.40 Å, d_m 2.20, *Z* 2, d_c 2.25, spacegroup $P6_3/mc$. Intensity data for both compounds were obtained from Weissenberg photographs of layers *hk0–hk7*. Those for the chloride were taken with MoK_α radiation and intensities estimated photometrically, whilst those for the bromide were taken with CuK_α radiation (decomposition occurred with MoK_α), and estimated visually. The structures were solved by Patterson and Fourier techniques and refined by the method of least squares. At the present time, the *R* factors are 0.07 (132 independent reflections, 13 parameters) for the dichloride and 0.10 (134 independent reflections, 17 parameters) for the dibromide. Isotropic temperature factors have been used so far.

The structures found are as seen in Fig.1 which shows the views down the *a* axes of the unit cells. Relevant bond lengths are included in this diagram. Apart from the confirmation of the difference between the two structures, the most interesting feature is the indication of apparent halogen–halogen interactions.

In the dichloride structure, the contact distance between the neighbouring chlorine atoms on the three-fold axis is 3.34(4)Å**, which is to be compared with an expected Van der Waals contact of about 3.6 Å[3]. A similar situation occurs, but to a lesser degree, in the structures of the trimethylantimony dihalides[4], with which Me_3AsCl_2 is structural. The presence of weak Cl–Cl interactions might account for the

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*Present address: Donnan Laboratories, Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, Grove Street, P.O. Box 147, Liverpool, L69 3BX (Great Britain).

**e.s.d's are given in parentheses throughout.

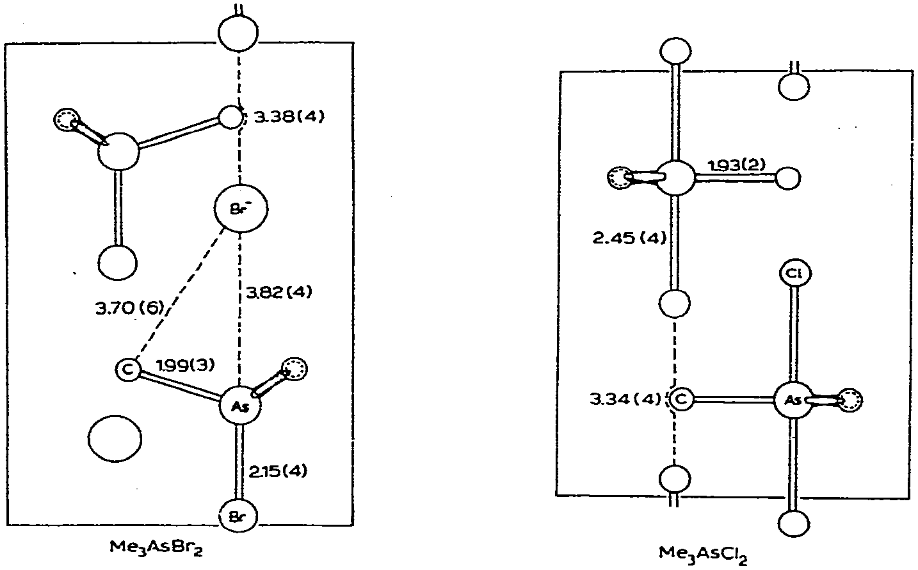

Fig.1. Structures of Me_3AsBr_2 and Me_3AsCl_2.

length of the As–Cl bond, which is longer than expected (As–Cl in $AsCl_3$ [5] is 2.161(4) Å) even when allowance is made for the change in geometry. For example, Sb–Cl is 2.34(3) Å in $SbCl_3$ [6] and 2.43(3) for the axial bonds in $SbCl_5$ [7].

In the dibromide structure, there exists an apparent bromine–bromide interaction as shown by a contact distance of 3.38(4) Å. (Sum of the Br^- ionic radius[3] and Br Van der Waals radius[3] is 3.9 Å. In this case, the As–Br bond is rather short (As–Br is 2.33(2) Å in $AsBr_3$ [8]), but this will be affected somewhat by the disordering of the cation which seems to be present (carbon atom temperature factors refine to negative values). In addition, bond lengths in positive ions of this sort tend to shorten. For example, P–Cl in $(PCl_4{}^+)$ [9] is 1.91 Å, in PCl_5 [7] is 2.04 Å (for equatorial bonds).

The implication of these results, together with those from our studies on related compounds, will be discussed in detail in a future publication[10].

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