

A Novel Arsenic Co-ordination

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THE existence of a one-sided fourfold co-ordination of trivalent antimony, first suggested by Edstrand,¹ has recently been confirmed by a number of structure determinations. Thus it is found in β -Sb₂O₄,² SbNbO₄³ (in a distorted form), and in two racemic tartrates, (\pm) -(NH₄)₂[Sb₂(C₄H₄O₆)₂].4H₂O⁴ and K[Sb(C₄H₄O₇)]. $\frac{1}{2}$ H₂O.⁵ The presence of such a co-ordination in a compound of trivalent arsenic is now reported.

Potassium di-*o*-phenylenedioxyarsenate(III),⁶ K[As(C₆H₄O₂)₂], is monoclinic and all crystals examined have proved to be twinned on (100) with *b*, *c* in common. The unit-cell dimensions are $a = 11.024 \pm 0.005$, $b = 6.284 \pm 0.002$, $c = 8.770 \pm 0.003$ Å, $\beta = 99^\circ 57' \pm 4'$, $U = 598.4$ Å³, $D_{\text{obs}} = 1.84$ g.cm.⁻³, $Z = 2$, $D_{\text{calc}} = 1.83$ g.cm.⁻³.

The structure has been determined from 801 independent reflections, obtained with Cu-*K* α radiation and visually estimated. Least-squares refinement, using isotropic temperature factors, has now reached $R = 0.059$. The space group is *Pc*, although the (001) projection is very nearly centrosymmetric.

Figure 1 shows that the structure consists of [As(C₆H₄O₂)₂]⁻ and K⁺ ions linked together to form infinite sheets in the *b*, *c* plane, the separate sheets being held together by van der Waals' forces. The twinning is caused by occasional mistakes in stacking of the sheets.

The co-ordination about As^{III}, seen in Figure 2, shows a very marked resemblance to that about Sb^{III} in β -Sb₂O₄.² The angles α and β are rather wider than the corresponding ones in β -Sb₂O₄;

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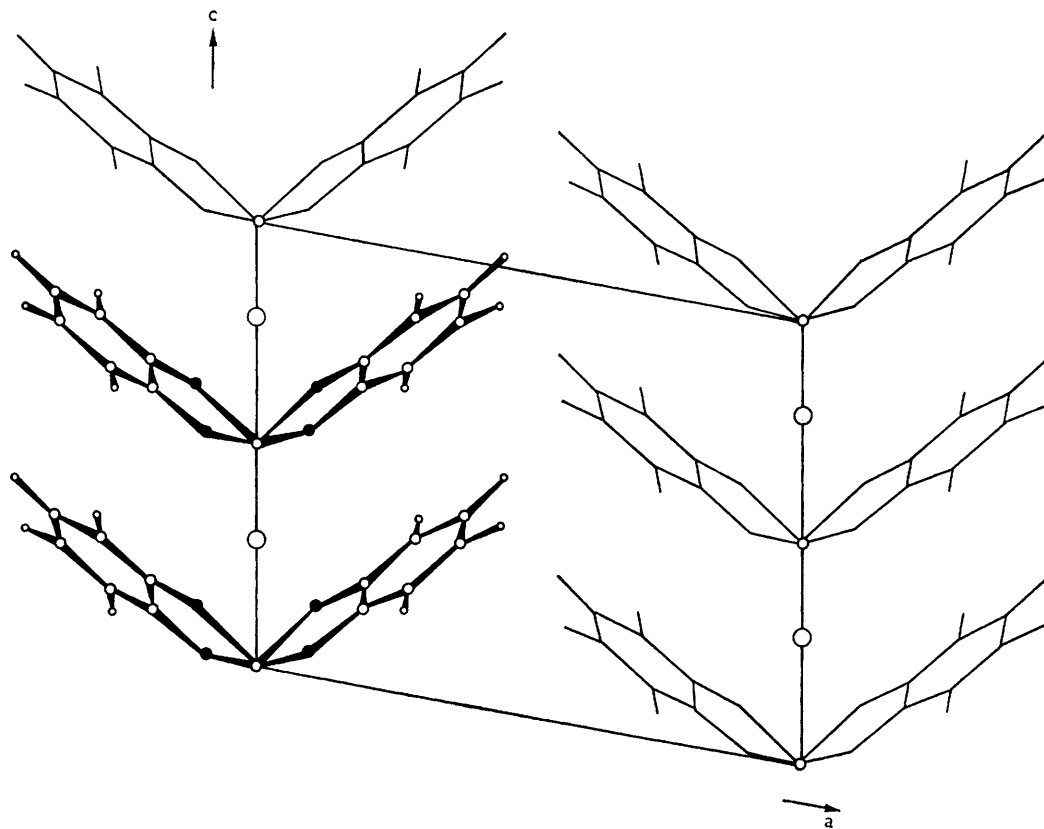


FIGURE 1 (b). $[0\bar{1}0]$ Projection of $K[As(C_6H_4O_2)_2]$.

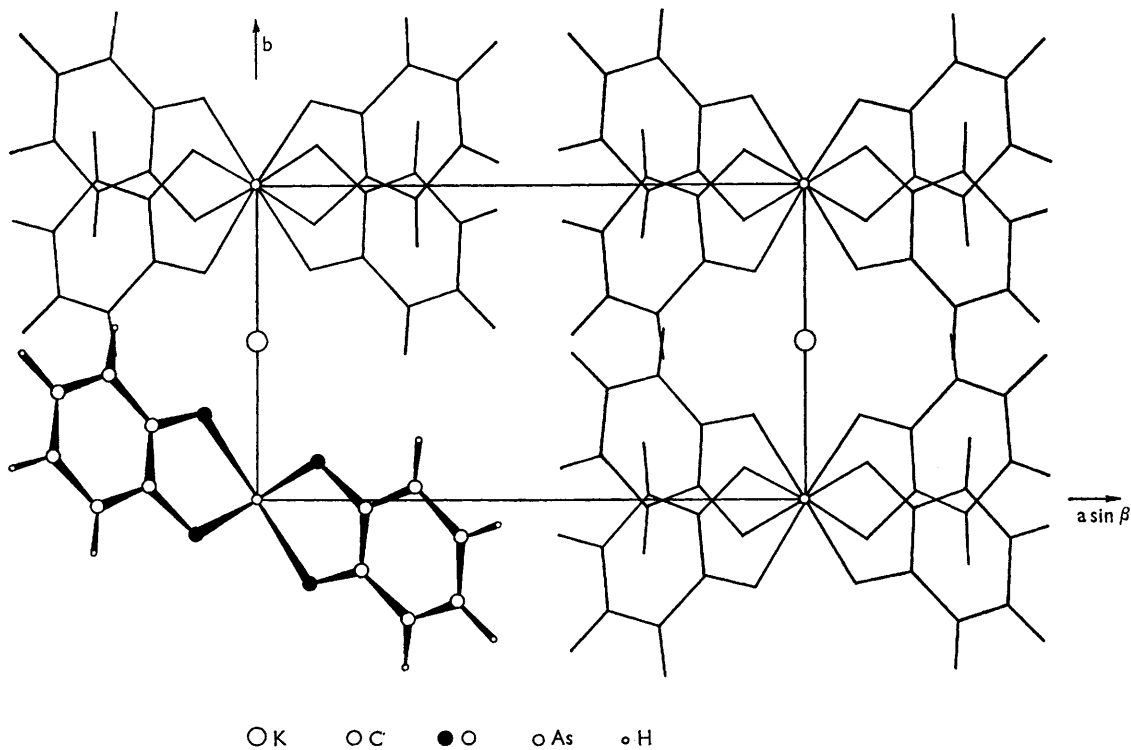


FIGURE 1 (a). $[001]$ Projection of $K[As(C_6H_4O_2)_2]$ (one anion above the origin has been removed for sake of clarity).

this, however, is a consequence of the smaller size of As^{III} compared to Sb^{III} , and therefore shorter As—O bond lengths. The arrangement of the four oxygen atoms relative to each other is very similar in both structures. In both cases two

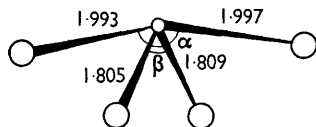


FIGURE 2

As^{III} co-ordination. $\alpha = 166.2^\circ$, $\beta = 101.5^\circ$. (Standard deviation of bonds is ~ 0.007 Å, and of angles $\sim 0.3^\circ$).

bonds are about 0.2 Å longer than the other two. The potassium is co-ordinated to six oxygen atoms at distances between 2.75 — 3.06 Å. There are no unusual features in the organic part of the anion.

Arsenic is not usually thought of as possessing a stereochemically-active inert pair. In this structure, however, it seems reasonable to assume that the inert pair forms the fifth apex of a distorted trigonal bipyramid. The lone-pair-bond-pair repulsion⁷ causes the oxygen atoms to move away from the lone pair until they come into contact with each other at distances 2.6 — 2.8 Å to form a rather distinctive arrangement.

(Received, November 24th, 1965; Com. 736.)

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