

Europium–Arsenic  $\text{Eu}_2\text{As}_2$ : a Single-Crystal Structure Refinement\*

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**Abstract.**  $\text{Eu}_2\text{As}_2$ , hexagonal,  $P\bar{6}2m$  ( $D_{3h}^3$ );  $Z = 3$ , F.W. 453.7;  $a = 8.154$  (1),  $c = 6.137$  (1) Å,  $V = 353.4$  Å<sup>3</sup>;  $D_m = 6.41$ ,  $D_x = 6.40$  g cm<sup>-3</sup>;  $\mu = 410.7$  cm<sup>-1</sup>. Diffractometer data from a spherical crystal ( $r = 145$  μm, 9078 measurements with  $2\theta \leq 90^\circ$ , 85% statistically observed, Mo  $K\alpha$ , graphite monochromator) gave  $R = 6.1\%$  for 887 independent observed  $hkl$  when corrected for absorption and refined by full-matrix least squares with allowance for anomalous dispersion. The structure is of the  $\text{Na}_2\text{O}_2$  type (Föppl, 1957) with trigonal-prismatic coordination of each Eu atom to six As atoms (Eu–As 3.09–3.18, average 3.14 Å, a distance which indicates divalent Eu) and each As atom octahedrally coordinated to six Eu plus two As atoms, one at  $\sim 3.6$  and another at  $\sim 2.5$  Å. Thus the As atoms occur in pairs, with the shorter As–As distances (2.46 or 2.56 Å) comparable to that observed in metallic arsenic (2.52 Å). The  $\text{Na}_2\text{O}_2$  structure, characterized by octahedra sharing faces, allows close approach of the central atoms, and differs in this way from the rock-salt structure of other rare-earth pnictides, in which octahedra share edges.

**Introduction.** Fragments from an ingot of composition  $\text{Eu}_{1.25}\text{As}$  which had been cycled 50 times through the peritectic temperature (975–1000°C, 160 min/cycle) were ground into spheres, and after many trials one specimen with a diameter of about 140 μm gave satisfactory Laue photographs. Intensity data were collected on a four-circle computer-controlled diffractometer using local programs (for details see Wang, Gabe, Calvert & Taylor, 1976). The lattice parameters, obtained by centring 35  $hkl$  reflexions

with  $2\theta$  between 40 and 47°, were  $a = 8.1527$  (8),  $b = 8.1536$  (8),  $c = 6.1375$  (4) Å and  $\alpha = 89.995$  (7),  $\beta = 90.007$  (7),  $\gamma = 120.001$  (7)° when refined as triclinic. The hexagonal values used in this structure refinement were  $a = 8.154$  (1),  $c = 6.137$  (1) Å; values reported for powder specimens are  $a = 8.1575$  (7),  $c = 6.1378$  (5) Å (Ono, Hui, Despault, Calvert & Taylor, 1971) and  $a = 8.150$ ,  $c = 6.135$  Å (Iandelli & Franceschi, 1973). During the alignment procedure a sphere of data with  $2\theta < 30^\circ$  was collected and it was found that the intensity distribution appeared to be monoclinic. The lattice parameters, related by the transformation 1,0,0/1,2,0/0,0,1 were  $a = 8.1536$  (7),  $b = 14.1208$  (3),  $c = 6.1375$  (3) Å,  $\beta = 90.003$  (6)°, and thus the unique monoclinic axis ( $b$ ) was not parallel to  $c$  hexagonal. Three-quarters of a sphere of data were collected using a  $\theta$ – $2\theta$  scan technique up to  $2\theta = 90^\circ$ . The experimental control and all refinement calculations were carried out on the laboratory PDP-8 computer (for details see Wang, Gabe, Calvert & Taylor, 1976); 9078 measurements were made, of which 85% were statistically taken as observed at the 10% significance level; these were reduced to 2570 and 887 independent observed  $hkl$  values for the monoclinic and hexagonal cells respectively. These were corrected for Lorentz–polarization and absorption [ $\mu R = 5.96$  (*International Tables for X-ray Crystallography*, 1959)]. The internal consistency between symmetry-related reflexions ( $= \Sigma \Delta / \Sigma I$ ) was 3.5%. A statistical test clearly showed a non-centric distribution and there were no systematically absent reflexions for the hexagonal cell. Two refinements were carried out based on a trial structure derived from the Patterson map. The first refinement, in  $Cm$ , gave  $R_1 = 6.2\%$  and  $R_2 = 5.8\%$ , and a second refinement in  $P\bar{6}2m$  refined to the values of Table 1 with  $R_1 = 6.1\%$  and

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Table 1. Fractional positional coordinates ( $\times 10^4$ ) and thermal parameters (Å<sup>2</sup>  $\times 10^4$ )

	$x$	$y$	$z$	$B_{11}$ *	$B_{33}$	$B_{12}$	$B_{\text{iso}}$ †
Eu(1)	3110 (3)	0	0	38 (2)	69 (3)	42 (4)	84 (1)
Eu(2)	6461 (3)	0	$\frac{1}{2}$	38 (2)	76 (4)	44 (4)	87 (1)
As(1)	0	0	2992 (9)	46 (4)	73 (9)	40 (0)	94 (4)
As(2)	$\frac{1}{3}$	$\frac{2}{3}$	2090 (5)	38 (3)	45 (6)	43 (0)	86 (3)

\*  $B_{11} = B_{22}$ ;  $B_{31} = B_{23} = 0$ . † From isotropic refinement ( $\times 10^3$ ).

$R_2 = 5.8\%$  for 887 independent observed  $hkl$ .† The two sets of coordinates were not statistically different. The largest shift in the last cycle was  $0.002 \text{ \AA}$  and represented  $0.3\sigma$ . There was no significant detail in the corresponding difference map and it was concluded that the compound was stoichiometric. Further, the originally observed monoclinic intensity distribution, which was confirmed in the full set of data, was ascribed to non-sphericity of the specimen; calculations based on the observed differences in radii showed this to be possible (e.g. at  $\theta = 15^\circ$ , for  $r_1 = 0.0063$  and  $r_2 = 0.0073 \text{ cm}$ ,  $A^*$  varies by  $30\%$ ).

**Discussion.** The equiatomic phase  $\text{EuAs}$  (Ono, Hui, Despault, Calvert & Taylor, 1971) does not possess the rock-salt structure observed for the other known rare-earth (RE) pnictides (Iandelli, 1960; McMasters & Gschneidner, 1964; Taylor, Calvert, Despault, Gabe & Murray, 1974). A structure of the  $\text{Na}_2\text{O}_2$  type was assigned by Ono, Hui, Despault, Calvert & Taylor (1971)‡ on the basis of the powder pattern and confirmed by Iandelli & Franceschi (1973), also from powder patterns. A full structure analysis, based on single-crystal data, was therefore thought to be desirable.

The rock-salt structure is characterized by sixfold octahedral coordination for both atoms, with the octahedra of any one type sharing edges with adjacent octahedra of the same type.  $\text{EuAs}$  with the  $\text{Na}_2\text{O}_2$ -type structure, is characterized by trigonal-prismatic coordination of Eu by six As atoms and coordination of As by six Eu atoms arranged octahedrally, plus two As atoms. The feature which distinguishes the rock-salt and  $\text{Na}_2\text{O}_2$ -type structures is that, in the latter, adjacent octahedra share faces, thus bringing the central atoms within bonding distance. Near-neighbour diagrams (Pearson, 1968) show these bonds to be the dominant feature in this structure type.

As(1) atoms form a  $3^6$  net ( $z = \pm 0.2993$ , mesh size =  $8.15 \text{ \AA}$ ) while the As(2) atoms form a  $6^3$  net ( $z = \pm 0.2098$ , mesh size =  $4.71 \text{ \AA}$ ). Both As atoms have very similar nearest-neighbour environments (Table 2) but different second-nearest-neighbour environments. The As(1) atom ( $z \approx 0.30$ ) has a planar hexagon of As(2) atoms  $4.74 \text{ \AA}$  distant ( $\Delta z \approx -0.09$ ), with the short As(1)—As(1) distance ( $2.45 \text{ \AA}$ ) normal to this plane and in the opposite  $z$  sense ( $\Delta z \approx +0.40$ ), whereas the As(2) atom ( $z \approx 0.21$ ) is associated with a buckled six-membered ring composed of three As(2) atoms at  $4.71 \text{ \AA}$  in the same  $z$  plane plus three As(1) atoms at  $4.74 \text{ \AA}$  ( $\Delta z \approx +0.09$ ), and the short

As(2)—As(2) distance ( $2.56 \text{ \AA}$ ) again occurs in the opposite  $z$  direction ( $\Delta z \approx -0.42$ ). Although the difference in these short As—As distances is not statistically significant, it may well be due to a second-neighbour effect.

The short As—As distances are comparable to the distance in metallic As ( $2.517 \text{ \AA}$ ) so that As atom pairs can be written formally as  $[\text{As—As}]^{4-}$  and the whole structure as  $\text{Eu}_2\text{As}_2$ . Thus  $\text{EuAs}$  can be described as a polyanionic structure of the form  $\text{M}^{II}\text{X}^{\text{V}}$  with the anions occurring in pairs, as in the (8- $N$ ) elements of the iodine family (Hulliger & Mooser, 1965), analogous to the situation in the CdSb-type structure (Almin, 1948). The occurrence of  $\text{EuN}$  and  $\text{EuP}$  containing  $\text{Eu}^{3+}$  (Gschneidner, 1969) with the rock-salt structure indicates that the smaller, more electronegative N and P atoms can overcome the tendency of Eu to adopt the  $\text{Eu}^{2+}$  state. From this, one would expect that in  $\text{EuSb}$  and  $\text{EuBi}$  (if they occur) Eu will be divalent and that some Sb—Sb, Bi—Bi bonding distances will be present.

Gschneidner (1969) calculated the promotion energy of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  to be  $23 \text{ kcal/g atom Eu}$  and discussed the general factors relating to the formation of divalent Eu. The observations given here are in general accord with Gschneidner's analysis. More recently, Bayanov (1975) calculated this promotion energy to be  $22 \text{ kcal/g atom Eu}$  and predicted the valence state of Eu, when alloyed with another element, as a function of the atomic number of the other element. His analysis correctly predicts divalency for Eu in  $\text{EuTe}$  but is incorrect for  $\text{EuS}$ ,  $\text{EuSe}$ ,  $\text{EuAs}$  ( $\text{Eu}^{3+}$  predicted) and  $\text{EuP}$  ( $\text{Eu}^{2+}$  predicted). The RE—As distances in the RE arsenides (containing trivalent RE atoms), calculated with the data of Taylor, Calvert, Despault, Gabe & Murray (1974), show the lanthanide contraction with a change of slope at the  $4f^7$  point (Eu), when plotted against atomic number. By interpolation, one would expect a Eu—As distance of  $2.95 \text{ \AA}$  in a hypothetical rock-salt structure, but the average observed Eu—As distance in  $\text{EuAs}$  ( $3.14 \text{ \AA}$ ) immediately suggests  $\text{Eu}^{2+}$ , which is confirmed by magnetic measurements (Iandelli & Franceschi, 1973).

Table 2. *Interatomic distances* ( $\text{\AA}$ ); *e.s.d.'s are 0.01 \AA or less*

Eu(1)		Eu(2)	
( $\times 2$ ) As(1)	3.131	( $\times 2$ ) As(1)	3.138
( $\times 4$ ) As(2)	3.092	( $\times 4$ ) As(2)	3.186
As(1)		As(2)	
( $\times 3$ ) Eu(1)	3.131	( $\times 3$ ) Eu(1)	3.092
( $\times 3$ ) Eu(2)	3.138	( $\times 3$ ) Eu(2)	3.186
As(1)	2.464	As(2)	2.572
As(1)	3.673	As(2)	3.565
Average values			
Eu(1)—As = 3.106		Eu(2)—As = 3.170	
As(1)—Eu = 3.135		As(2)—Eu = 3.139	

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31972 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

‡ The  $x$  values given for Eu in 3( $f$ ) and 3( $g$ ) correspond to the values for 3( $g$ ) and 3( $f$ ) in Table 1 of the present study.

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## 16-Demethoxycarbonyl-20-epiervatamine

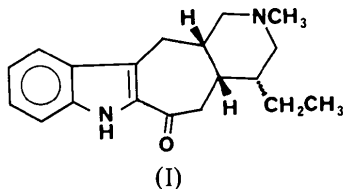
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**Abstract.**  $\text{C}_{19}\text{H}_{25}\text{N}_2\text{OBr}$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.212$  (4),  $b = 13.353$  (6),  $c = 14.217$  (7) Å,  $Z = 4$ ,  $M_r = 377.1$ ,  $d_x = 1.43$  g cm $^{-3}$ . Final  $R$  value: 0.078.

**Introduction.** The purpose of this investigation was to establish the molecular configuration of this alkaloid extracted from different species of *Hazunta* (Bui & Potier, unpublished). The X-ray analysis shows the compound to be 16-demethoxycarbonyl-20-epiervatamine (I) (Shafiee, Ahond, Bui, Langlois, Riche & Potier, 1976).



The stereochemistry of the related alkaloids ervatamine, epiervatamine and 19,20-dehydroervatamine has been recently determined (Husson, Langlois, Riche, Husson & Potier, 1973).

Preliminary photographs showed the crystals to be orthorhombic, space group  $P2_12_12_1$ . A crystal approximately  $0.1 \times 0.15 \times 0.3$  mm was used to measure the

cell parameters and intensities on a Philips PW 1100 four-circle diffractometer. Data were collected to a maximum  $\theta$  of  $50^\circ$  with graphite-monochromated  $\text{Cu K}\alpha$  radiation. ( $\lambda = 1.5418$  Å,  $\omega$ - $2\theta$  scan, scan width:  $1.5^\circ$ , scan speed:  $0.12^\circ$  s $^{-1}$ ; background was measured for 4 s on either side of the peak). Of the 2164 reflexions measured ( $hkl$  and  $\bar{h}\bar{k}\bar{l}$ ), 2055 had intensities above  $2\sigma(I)$  where  $\sigma(I)$  was the standard deviation derived from counting statistics. No correction for absorption was made.

The structure was solved by the heavy-atom method and refined by full-matrix least squares (ORFLS: Busing, Martin & Levy, 1962) minimizing  $\Sigma(F_o - |F_c|)^2/\sigma^2(F_o)$ . The temperature factors were anisotropic for Br and isotropic for C, N and O. The H atoms were included in their calculated positions. The scattering factors used for C, N, O and Br $^-$  were those of Doyle & Turner (1968) and for H, those of Stewart, Davidson & Simpson (1965). The component of the anomalous dispersion applied for Br was taken from *International Tables for X-ray Crystallography* (1968). All the observed reflexions ( $hkl$  and  $\bar{h}\bar{k}\bar{l}$ ), which had been indexed according to a right-handed set of axes, were used. Two refinements were performed corresponding to the possible enantiomorphs. The  $R$  values were:  $R(+)=7.8$ ,  $R(-)=8.3$ ,  $R_w(+)=10.3$ ,  $R_w(-)=10.7\%$ . Examination of several sensitive Bijvoet pairs indicated the correctness of the (+) enantiomorph.