

Structure of Trieuropium Triarsenide–Tantalum Oxide (1 : 1)*

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Abstract. $\text{Eu}_3\text{As}_3\cdot\text{TaO}$, orthorhombic, $Pnma$, $a = 6.327$ (1), $b = 10.620$ (1), $c = 12.804$ (1) Å, $U = 860.3$ Å³, $M_r = 877.6$, $Z = 4$, $D_x = 6.78$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 47.09$ mm⁻¹, $F(000) = 1475$. Diffractometer data gave $R = 4.5\%$ for 1211 independent observed reflections when refined by full-matrix least squares. The structure contains discrete slabs of trigonal $[\text{Eu}_3\text{As}_3]$ prisms. One sixth of these prisms are centred by a TaO group (Ta–O = 1.87 Å). Average Eu–Eu, Eu–As and Ta–As distances are 4.31, 3.16 and 2.45 Å, consistent with metallic radii, whereas Ta–O and Eu–O (2.49 Å) distances are indicative of significant ionic character.

Introduction. This work was undertaken to resolve a difficulty encountered in studies of the Eu–As system (Ono, Hui, Despault, Calvert & Taylor, 1971; Taylor, Calvert, Utsunomiya, Wang & Despault, 1978; Wang, Calvert, Taylor & Gabe, 1978). Samples with compositions close to 50 at.% As, which were annealed in tantalum containers at temperatures between 1373 and 1573 K, were found to contain minor amounts of a phase which could not be placed on the Eu–As phase diagram. Although it was suspected to be a contaminant phase, prior to this structure analysis no conclusive proof of its nature was obtained either by varying conditions of synthesis (annealing temperature, crucible material, sample composition) or by chemical analysis, because it was never obtained as a single phase. A few well formed shiny metallic crystals were obtained from a sample of overall composition $\text{EuAs}_{1.05}$ which was slow-cooled after annealing at 1473 K in a tantalum container. The crystals were laths (elongated along a) or (001) tablets, with {011} and {010} also observed. Gandolfi and Guinier photographs confirmed that these were the desired phase but no single-phase powder pattern suitable for publication was obtained.

Intensity data were collected from a lath-shaped crystal $\sim 0.06 \times 0.08 \times 0.12$ mm using a four-circle

computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.70932$ Å) and local programs (for details see Wang, Gabe, Calvert & Taylor, 1976; Larson & Gabe, 1978). The space group was determined from precession photographs ($0kl$: $k + l = 2n$; $hk0$: $h = 2n$) and intensity statistics to be $Pnma$. The lattice parameters were measured by centring 45 reflections with 2θ in the range 56 – 65° . Two sets of reflections hkl and $\bar{h}\bar{k}\bar{l}$ with $2\theta < 65^\circ$ were collected with a θ – 2θ scan using the profile-analysis technique (Grant & Gabe, 1978). The scan range was varied as a function of θ (2θ range = $1.4^\circ + 0.7^\circ \tan \theta$) to account for wavelength dispersion; 3272 measurements were made, equivalent to 1632 independent reflections of which 1211 were taken as observed [$I > 2\sigma(I)$]; these were corrected for Lorentz, polarization and absorption effects (Gabe & O'Byrne, 1970). Transmission coefficients ranged from 0.05 to 0.14. Equivalent reflections were averaged ($\sum \Delta I / \sum I = 0.05$). All calculations were carried out on the laboratory computer using the NRC-PDP-8 system of programs (Larson & Gabe, 1978). The structure was refined, using the 1211 observed reflections with allowance for anomalous dispersion and isotropic extinction ($g = 3.2 \times 10^{-7}$; Larson, 1969), by anisotropic full-matrix least squares to $R_1 = 0.045$ and $R_2 = 0.050$, where $R_1 = (\sum | \Delta F | / \sum F_o)$ and $R_2 = (\sum w | \Delta F |^2 / \sum w F_o^2)^{1/2}$ and $w = 1 / \sigma^2(F_o) = 1 / [\sigma^2(F_o)_{\text{counts}} + (0.03 F_o)^2]$. Starting coordinates for Eu and As atoms were derived from a three-dimensional Patterson map. Ta and O sites were located from the heights of peaks in difference maps and their identities confirmed by the temperature factors derived on refinement. The final difference Fourier map contained no significant detail. A microprobe analysis

Table 1. Atomic fractional coordinates ($\times 10^4$) and equivalent B values

	x	y	z	B_{eq} (Å ²)
Eu(1)	7529 (1)	425 (1)	1283 (1)	1.12 (2)
Eu(2)	2709 (2)	7500	1275 (1)	1.06 (3)
Ta	1595 (1)	2500	495 (1)	0.82 (2)
As(1)	7659 (3)	7500	1374 (1)	1.09 (6)
As(2)	2625 (2)	455 (1)	1237 (1)	1.14 (5)
O	3639 (20)	2500	4453 (10)	1.14 (16)

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Table 2. *Interatomic distances (Å)*

Eu(1)—Eu(1)	4.407 (2)	Ta—2× Eu(1)	3.534 (1)
—2× Eu(1)	4.441 (2)	—2× Eu(1)	3.891 (1)
—Eu(2)	3.950 (2)	—Eu(2)	3.543 (2)
—Eu(2)	4.353 (1)	—Eu(2)	4.257 (2)
—Eu(2)	4.409 (1)	—As(1)	2.439 (2)
—Ta	3.534 (1)	—2× As(2)	2.458 (1)
—Ta	3.891 (1)	—O	1.87 (1)
—As(1)	3.109 (1)		
—As(2)	3.103 (1)	As(1)—2× Eu(1)	3.110 (1)
—As(2)	3.176 (2)	—Eu(2)	3.010 (2)
—As(2)	3.225 (1)	—Eu(2)	3.134 (2)
—As(2)	3.361 (2)	—Eu(2)	3.198 (2)
—O	2.50 (1)	—Ta	2.439 (2)
Eu(2)—2× Eu(1)	3.950 (2)	As(2)—Eu(1)	3.103 (1)
—2× Eu(1)	4.353 (1)	—Eu(1)	3.176 (2)
—2× Eu(1)	4.409 (1)	—Eu(1)	3.225 (1)
—2× Eu(2)	4.455 (2)	—Eu(1)	3.361 (2)
—Ta	3.543 (2)	—Eu(2)	3.139 (1)
—Ta	4.257 (2)	—Ta	2.458 (1)
—As(1)	3.010 (2)		
—As(1)	3.134 (2)	O—2× Eu(1)	2.50 (1)
—As(1)	3.198 (2)	—Eu(2)	2.48 (1)
—2× As(2)	3.139 (1)	—Ta	1.87 (1)
—O	2.48 (1)		
		Average Eu—Eu	4.31
		Eu—As	3.16
		Ta—As	2.45

of the crystal used, with standards of Ta_3As and Eu_4As_3 , gave an analysis equivalent to $Eu_{3.02}As_{3.03}Ta_{0.97}O_{0.97}$ (Owens, 1978), so that the stoichiometric formula was accepted. The final parameters are given in Table 1, interatomic distances in Table 2.*

Discussion. The structure contains 4^23^3 networks of Eu and As atoms at $x = \frac{1}{4}, \frac{3}{4}$ (Fig. 1) stacked directly one above the other with Eu and As atoms alternating along each row parallel to *a* (Fig. 2). Trigonal $[Eu_3As_3]$ prisms are thus formed which share triangular faces and two out of three rectangular faces to make slabs perpendicular to the *c* axis. The unshared rectangular faces of the prisms in adjacent slabs face each other and outline $[Eu_4As_4]$ distorted cubes. In any row of prisms every third prism is larger than the other two and every alternate one of these is centred by a TaO 'group' (Fig. 2). Alternatively one can say that the O atom is tetrahedrally bonded to $3Eu + 1Ta$ (Table 2) and the Ta atom is also tetrahedrally bonded to $1O + 3As$, suggesting as a possible formulation: $Eu_3^4+O^{2-}Ta^{5+}As_3^{3-}$. The observed distances for Eu—Eu, Eu—As and Ta—As (4.31, 3.16 and 2.45 Å respectively) are close to metallic values observed in similar compounds [4.15 and 3.14 Å in Eu_2As_2 (Wang, Gabe,

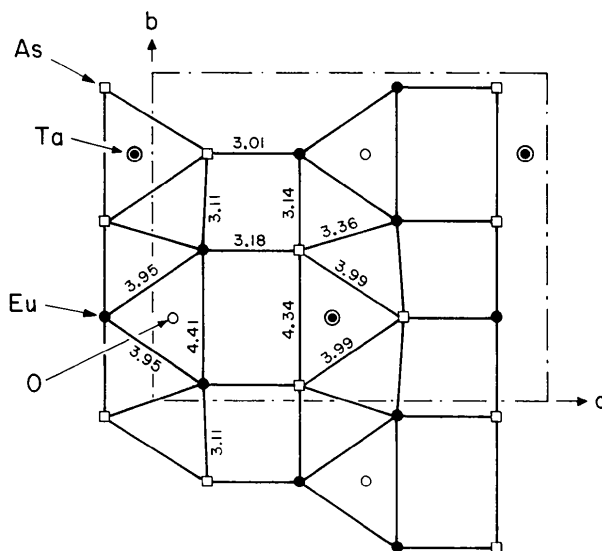


Fig. 1. The section of the Eu_3As_3TaO structure at $x \sim \frac{1}{4}$. The Ta and O atoms lie outside the $x = \frac{1}{4}$ plane. The atoms at $x = \frac{1}{4}$ form 4^23^3 networks. The distances given serve to distinguish the larger and smaller trigonal prisms.

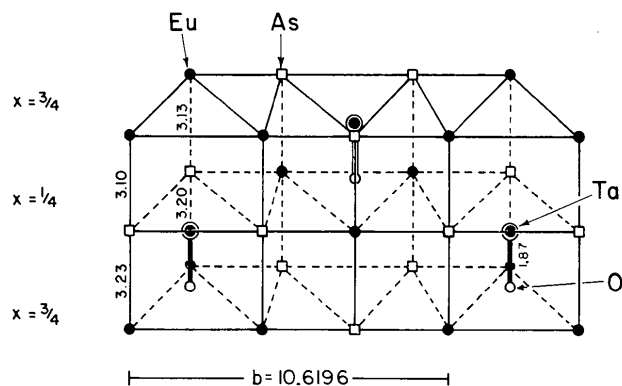


Fig. 2. One discrete slab of trigonal prisms showing the alternation of Eu and As atoms and the arrangement of the TaO groups.

Calvert & Taylor, 1977) and 2.43 Å in TaAs (Murray, Taylor, Calvert, Wang, Gabe & Despault, 1976)], while the value for Eu—O (2.49 Å) is close to that in EuO (2.57 Å) (Bärnighausen, 1966). The value for Ta—O is very close to that of TaO gas (1.827 Å; *International Tables for X-ray Crystallography*, 1962). Thus a simple description is that of a largely metallic framework with a TaO 'gas molecule' inserted in a chemically and dimensionally favourable location.

One referee raised the question of the relationship between the lattice of Eu_2As_2 and that of Eu_3As_3TaO . The previous description of Eu_2As_2 (Wang, Gabe, Calvert & Taylor, 1977), chosen to emphasize the similarity with the rock-salt structure, is based on

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34771 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

discrete columns of [AsEu₆] octahedra sharing faces. An alternate description is in terms of slabs of [As₆] trigonal prisms, based on the 3⁶ As atom nets with mesh size ~4.7 Å and centred by Eu atoms. This can be visualized from Fig. 2 of the present paper if we imagine the trigonal prisms as formed by As atoms only with an Eu atom centring alternate prisms, e.g. every second prism in the bottom row and the other ones in the row above. In Eu₂As₂ such slabs are contiguous and all faces are shared. In Eu₃As₃.TaO the slabs are discrete, and the layers are mixed-atom layers as opposed to the single-atom layers in Eu₂As₂. There is thus no simple lattice relationship between the two.

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Structure d'un Orthoarsénate Acide de Cadmium: CdH₁₀(AsO₄)₄

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Abstract. CdH₁₀(AsO₄)₄, triclinic, $P\bar{1}$, $a = 5.69$ (5), $b = 7.42$ (4), $c = 8.60$ (6) Å, $\alpha = 105.17$ (1), $\beta = 95.13$ (5), $\gamma = 91.85$ (8)°, $Z = 1$, $d_x = 3.25$ Mg m⁻³. The crystal structure has been determined and refined to a final R value of 0.056 with 1706 reflexions. The structure consists of CdO₆–AsO₄ chains along a , held together by hydrogen bonds.

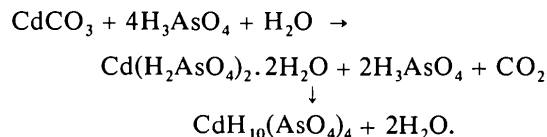
Introduction. En dissolvant du carbonate de cadmium dans une solution fortement concentrée en acide arsénique, on voit apparaître au bout de deux à trois jours des cristaux de Cd(H₂AsO₄)₂.2H₂O.

Ce composé, abandonné dans la solution-mère à la température ambiante, se transforme au bout d'une dizaine de jours, après évaporation totale de l'eau.

Les cristaux de ce composé se présentent sous forme de lames allongées, translucides et poussent en touffes. Ce composé est hygroscopique. En dehors de la solution-mère au bout de quatre à cinq jours, il redonne Cd(H₂AsO₄)₂.2H₂O. Au contact de l'eau, ce sel se transforme rapidement en orthoarsénate diacide de cadmium dihydraté.

L'étude structurale nous a conduit à attribuer à ce composé la formule chimique suivante: CdH₁₀(AsO₄)₄. L'analyse chimique nous a confirmé par la suite cette formule: CdO 19%, As₂O₅ 68%, H₂O 13%.

Le mécanisme réactionnel serait donc:



Ce composé, qui n'a jamais été signalé à notre connaissance, vient donc enrichir la série des monoarsénates acides de cadmium: Cd₅H₂(AsO₄)₄.4H₂O (Averbuch-Pouchot, 1974; Demel, 1879; Flakwosky, 1868; Klemp & Gyulay, 1921), CdHAsO₄.H₂O (Coloriano, 1886; Demel, 1879; Ephraïm & Rosseti, 1945; Flakwosky, 1868; Klement & Haselberg, 1964), et Cd(H₂AsO₄)₂.2H₂O (Averbuch-Pouchot, 1974; De Schulten, 1889).

La maille cristalline a été déterminée directement au diffractomètre automatique Philips PW 1100. Le