

Table 3. *M—N and M—O average bond distances (Å) and ionic radii (Å) (Shannon, 1976) for the iron(III), chromium(III), nickel(II) and copper(II) dipicolinate complexes*

<i>M</i>	<i>M—N</i>	<i>M—O</i>	Ionic radii	
Fe ^{III}	2.05	2.02	0.645	High spin
			0.550	Low spin
Cr ^{III}	1.97	2.00	0.615	
Ni ^{II}	1.97	2.10	0.692	
Cu ^{II}	1.90	2.04	0.730	

The title compound was prepared under hydrothermal conditions. Stoichiometric amounts of ferric hydroxide and dipicolinic acid were intimately mixed and suspended in water in a sealed Pyrex tube and allowed to react at 423 K for 24 h. The resultant green crystals were stable to air exposure. The structure was solved by the Patterson method and successive Fourier maps. H atoms were found from difference Fourier syntheses. All calculations were performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) on a VAX 6310 computer.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54982 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1001]

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Structure of a New Natural Tungstate Arsenate, [Ca₂Y(AsO₄)(WO₄)₂],[†] Structurally Related to Scheelite

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Abstract

The structure of the new natural tungstate arsenate [Ca₂Y(AsO₄)(WO₄)₂] found in the Alpine fissures of the Pizzo Cervandone Area (Ossola Valley, Italy) is reported. It conforms to the scheelite-type structure and consists of layers with composition YAsO₄ and CaWO₄ stacked in an orderly manner along [001] in the molar ratio 1:2.

Comment

The region of Pizzo Cervandone in the Central Alps (Italy/Switzerland) is particularly interesting because of its Alpine fissure minerals. This area is characterized by a striking positive arsenic anomaly (Graeser, 1965) which gives rise to a number of unique or unusual arsenic minerals in the gneiss fissures. A single specimen of the new mineral investigated here was found in 1990 by the mineral collector Fausto Parani, in the Italian side of this region (Alpe Devero – Ossola Valley). It occurs as small creamy yellow crystals (up to 3 mm), with elongated bipyramidal habit, closely resembling scheelite (CaWO₄). A quantitative wavelength-dispersion microprobe analysis on the sample revealed the presence of W, Ca, As and Y as major constituents, together with minor quantities of heavy lanthanides (Er and Yb) and traces of Nb and U. The unit-cell parameters and the symmetry of the

[†] Mineral submitted to IMA (International Mineralogical Association) for approval 'as Paranite-(Y)'.

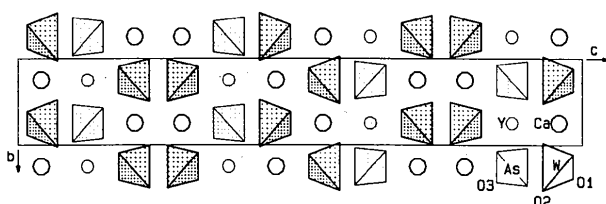


Fig. 1. Projection of the crystal structure of $[\text{Ca}_2\text{Y}(\text{AsO}_4)(\text{WO}_4)_2]$ along $[100]$ obtained by the program *POLIEDRI* (Pilati, 1990).

mineral are strictly correlated with those of scheelite [$a = 5.2429$ (3), $c = 11.3737$ (6) Å] (Hazen, Finger & Mariathasan, 1985), the c parameter being approximately three times the corresponding value for scheelite. A small contraction is observed in the a parameter with respect to scheelite. The space group, $I4_1/a$, is the same. All these observations led to a structural model which was successfully refined. This model derives from the content of three unit cells of scheelite, superimposed along $[001]$. It consists of layers with composition YAsO_4 ($c = \text{chernovite}$) and CaWO_4 ($s = \text{scheelite}$) stacked in an orderly manner along $[001]$, with stacking sequence $cs\text{sc}sc\text{sc}$. In this way a third of the Ca and the W atoms have been replaced by Y and As, without implying disorder.

The occupancy of W, Ca and Y was considered in the refinement to account for partial replacement of Y by heavier lanthanides, of W by Nb or As and of Ca by Y, as suggested by the chemical analysis.

The final atomic coordinates and thermal parameters with their e.s.d.'s are listed in Table 1. A perspective view of the crystal structure is shown in Fig. 1. Y and the AsO_4 groups lie on the $\bar{4}$ axis while Ca and the WO_4 groups on twofold crystallographic sites. Both Y and Ca are in eightfold coordination, the coordination polyhedron being a bisdisphenoid. Selected interatomic distances and angles are reported in Table 2. No unusual features are observed in the geometrical parameters of the structure.

Experimental

Crystal data

$[\text{Ca}_2\text{Y}(\text{AsO}_4)(\text{WO}_4)_2]$

$M_r = 803.68$

Tetragonal

$I4_1/a$

$a = 5.135$ (1) Å

$c = 33.882$ (5) Å

Cell parameters from 25 reflections

$\theta = 9.30\text{--}23.5^\circ$

$V = 893.4$ (4) Å³

$Z = 4$

$D_x = 5.975$ Mg m⁻³

Mo $K\alpha$

$\lambda = 0.71073$ Å

$\mu = 37.6$ mm⁻¹

$T = 293$ K

$0.15 \times 0.10 \times 0.05$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer

Variable scan speed

4281 measured reflections

$\theta_{\text{max}} = 35^\circ$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 8$

$l = -54 \rightarrow 54$

1405 independent reflections

840 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.027$

Refinement

Refinement on F

Final $R = 0.024$

$wR = 0.027$

$S = 1.104$

840 reflections

45 parameters

1 standard reflection

monitored every 150

reflections

intensity variation: 0.8%

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} = 0.01$

$\Delta\rho_{\text{max}} = 1.25$ e Å⁻³

$\Delta\rho_{\text{min}} = 0.75$ e Å⁻³

Extinction correction: none

An absorption correction was applied according to the procedure described in Demartin, Gramaccioli & Pilati (1992) for strongly absorbing crystals, *i.e.* by performing an empirical ψ -scan correction (North, Phillips & Mathews, 1968; $T_{\text{min}} = 0.38$, $T_{\text{max}} = 1.00$) followed by a *DIFABS* correction (Walker & Stuart, 1983; $T_{\text{min}} = 0.84$, $T_{\text{max}} = 1.23$). Scattering factors for neutral atoms and anomalous-dispersion corrections for scattering factors were taken from Cromer & Waber (1974) and Cromer (1974), respectively. All the computations were performed on a PDP 11/73 computer, using the *SDP-Plus Structure Determination Package* (B. A. Frenz & Associates, Inc., 1980).

Table 1. Fractional atomic coordinates with e.s.d.'s

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	Multiplicity	x	y	z	U_{eq} (Å ²)
Y	0.26	0.000	0.250	0.125	0.00898 (9)
As	0.25	0.500	-0.250	0.125	0.00842 (9)
W	0.45	0.000	-0.250	0.04679 (1)	0.01032 (4)
Ca	0.57	0.500	0.250	0.04167 (3)	0.0125 (3)
O(1)	1.00	0.2437 (8)	-0.1147 (8)	0.0160 (1)	0.0171 (8)
O(2)	1.00	0.1559 (7)	0.4784 (7)	0.0705 (1)	0.0158 (8)
O(3)	1.00	0.3220 (9)	-0.0340 (8)	0.0977 (1)	0.0205 (8)

Table 2. Selected interatomic distances (Å) and angles (°)

W—O(1) × 2	1.771 (4)	O(1)—W—O(1 ^{iv})	107.8 (2)
W—O(2) × 2	1.798 (4)	O(1)—W—O(2) × 2	104.7 (2)
		O(1)—W—O(2 ^{iv}) × 2	105.9 (2)
		O(2)—W—O(2 ^{iv})	126.9 (2)
As—O(3) × 4	1.709 (4)	O(3)—As—O(3 ^{iv}) × 4	107.0 (1)
		O(3)—As—O(3 ^v) × 2	114.5 (3)
Y—O(2) × 4	2.329 (4)	Y—O(3) × 4	2.391 (4)
Ca—O(1) × 2	2.449 (4)	Ca—O(2) × 2	2.335 (4)
Ca—O(1 ^{iv}) × 2	2.456 (4)	Ca—O(3) × 2	2.562 (4)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -\frac{1}{2} - y, z$; (iii) $-x, \frac{1}{2} - y, z$; (iv) $\frac{3}{4} + y, \frac{1}{4} - x, \frac{1}{4} - z$; (v) $1 - x, -\frac{1}{2} - y, z$; (vi) $1 - x, -y, -z$.

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Lists of observed and calculated structure-factor moduli and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55049 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1005]

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16-(*p*-Butoxybenzylidene)androsta-1,4-diene-3,17-dione

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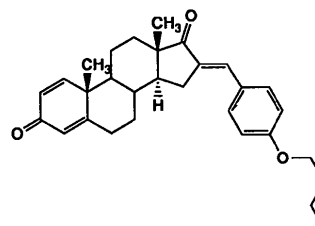
Abstract

The cyclohexa-1,4-dien-3-one ring in the androsta-1,4-dien-3-one skeleton adopts a nearly planar conformation. The conformation of the styryl ketone fragment slightly deviates from planarity. The crystals show significant second-order-harmonic generation and short cut-off wavelength for absorption.

Comment

One of the obstacles to the realization of organic materials for an effective second-order-harmonic generation (SHG) device of a diode laser is an undesirable tendency for molecules with a large SHG hyperpolarizability to have

a longer cut-off wavelength for light absorption (Itoh, Oono, Isogai & Kakuta, 1989; Prasad & Williams, 1991). In the course of our attempt to overcome this obstacle by molecular design (Oono, Itoh, Hamada, Isogai & Kakuta, 1990; Ogawa, Yoshimura, Takeuchi, Katritzky & Murugan, 1992), it was found that the title compound shows an appreciable deviation from this tendency. The basic idea for the design of the new molecule is that the styryl ketone fragment as a polarizable unit is incorporated into the steroidal skeleton as a chiral backbone unit.



The compound was readily obtained as noncentrosymmetric crystals from the condensation reaction of androsta-1,4-diene-3,17-dione with 4-butoxybenzaldehyde. It showed a powder SHG efficiency 6.7 times that of urea for a fundamental wavelength of 1.064 μm of an Nd^{3+} :YAG laser using the technique of Kurtz & Perry (1968) and showed no absorption at λ longer than 420 nm.

A search of the January 1992 Version of the Cambridge Structural Database (1992) revealed that this paper is the first report on the crystal structure of the compound with an androsta-1,4-diene fragment attached to the styryl unit. The bond lengths and angles of the androstadiene skeleton are essentially as expected. The cyclohexa-1,4-dien-3-one ring adopts a nearly planar conformation.

The dihedral angle between the benzene ring and the plane of the ethylene unit $\text{C16}=\text{C20}$ deviates slightly from 0° and the ethylene bond angle $\text{C16}=\text{C20}-\text{C21}$ is significantly larger than 120° . These features of the styryl ketone fragment geometry of the title compound are essentially the same as those of chalcones (Rabinovich & Shakked, 1974; Rabinovich, Schmidt & Shakked, 1973) and 2-benzyl-5-benzylidenecyclopentanones (Theocharis, Nakanishi & Jones, 1981).

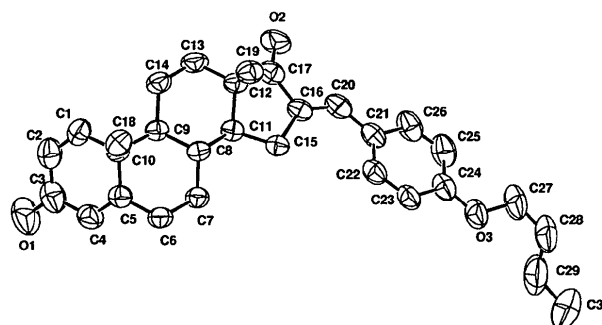


Fig. 1. Perspective view of the title compound.