

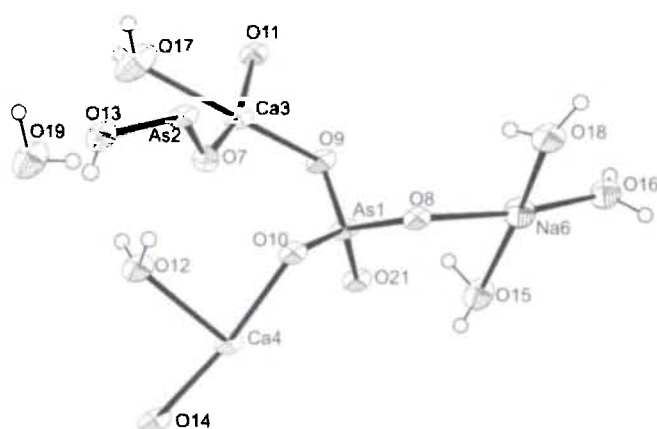
Crystal structure of dicalcium sodium monohydrogen diarsenate hexahydrate, $\text{Ca}_2\text{Na}[\text{HAsO}_4][\text{AsO}_4] \cdot 6\text{H}_2\text{O}$

A. Jiménez^I, J. D. Rodríguez^I, L. Torre-Fernández^{II}, M. Prieto^I and S. García-Granda^{*,II}

^I Universidad de Oviedo, Facultad de Geología, Departamento de Geología, Jesus Arias de Velasco s/n, 33005 Oviedo, Asturias, Spain

^{II} Universidad de Oviedo, Facultad de Química, Departamento de Química Física y Analítica, 33006 Oviedo, Asturias, Spain

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Abstract

$\text{As}_2\text{Ca}_2\text{H}_{13}\text{NaO}_{14}$, triclinic, $P\bar{1}$ (no. 2), $a = 6.680(5)$ Å, $b = 8.223(4)$ Å, $c = 12.537(3)$ Å, $\alpha = 73.46(5)^\circ$, $\beta = 78.89(4)^\circ$, $\gamma = 87.47(5)^\circ$, $V = 647.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.062$, $wR_{\text{ref}}(F^2) = 0.197$, $T = 293$ K.

Source of material

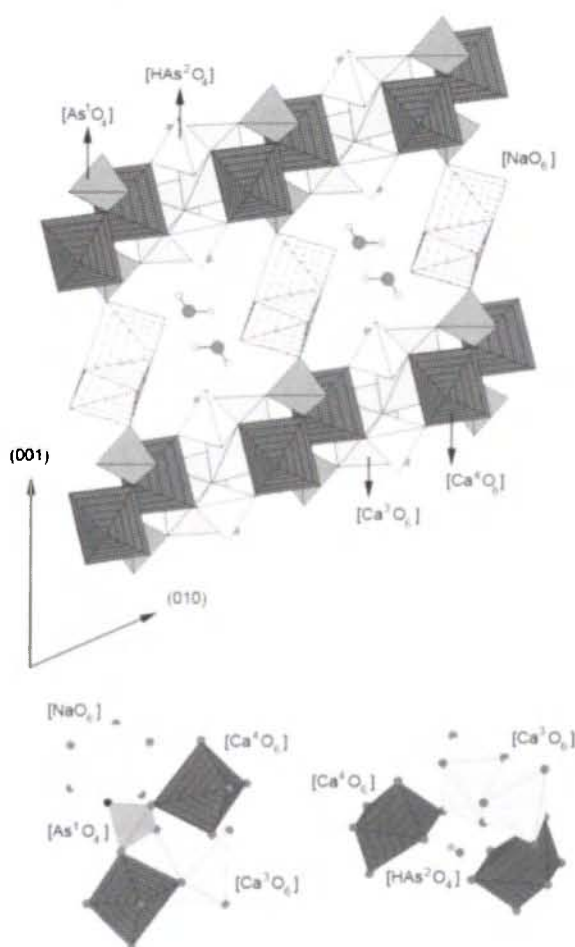
Crystallization of $\text{Ca}_2\text{Na}(\text{HAsO}_4)(\text{AsO}_4) \cdot 6\text{H}_2\text{O}$ was carried out by mixing CaCl_2 (0.01 M) and Na_2HAsO_4 (1 M) aqueous solutions in a thermostated (25(1) °C) polypropylene vessel. 50 cm³ of each parent solution were placed in the reacting vessel, which was then sealed with a polypropylene cap to avoid evaporation. After mixing, the pH reached a value of ca. 8.90. The obtained crystals are tabular (ca. 100 µm) with well-defined polygonal contours.

Experimental details

Hydrogen atoms were geometrically placed and refined using distance restraints. Odd anisotropic displacement parameters were found probably due to crystal size and shape. The range of Ca/As and Na/As ratios measured by EDS seems to exceed the analytical error, suggesting the possibility of a coupled substitution of $\text{Ca}^{2+} + \text{AsO}_4^{3-}$ for $\text{Na}^+ + \text{HAsO}_4^{2-}$.

Discussion

Although arsenic has been classified at the top of the priority list of the most hazardous substances [1], the crystal chemistry of numerous As-bearing compounds continues to be poorly known. Under oxidizing conditions As(V) is the most common form of arsenic in natural waters, with AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- and H_3AsO_4^0 being the prevailing aqueous species in different pH ranges. Immobilization of arsenate in the environment can occur by precipitation of low-solubility salts or by sorption on mineral surfaces. Precipitation of calcium arsenates has been proposed as a remediation method, and the interaction of As(V) with limestone has been widely studied [2]. This interaction leads to the formation of a series of calcium arsenate compounds, many of them with unknown XRD patterns [3]. At present there are over 20 different calcium arsenate compounds in the Powder Diffraction File, but the crystal structure has only been determined for a part of these compounds. The most complete research on the crystal-chemistry of these arsenates was carried out by Ferraris and co-workers [4–8], who studied the structures of a number of arsenates and hydrogen arsenates of calcium. According to these authors, the coexistence of arsenate groups with different protonation degrees is common in calcium arsenates as $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$ (guerinite and ferrarisite) and $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (sainfeldite). Formation (at pH ca. 8) of guerinite, sainfeldite, and the new arsenate $\text{NaCa}_2(\text{HAsO}_4)(\text{AsO}_4) \cdot 6\text{H}_2\text{O}$ was observed in a previous study [9] on the interaction of As(V) with gypsum, which is the origin of the present work.



* Correspondence author (e-mail: sgg@uniovi.es)

The crystal structure of NaCa₂(HASO₄)(AsO₄) · 6H₂O is formed by (001) layers consisting of [AsO₄] tetrahedra and [CaO₆] polyhedra. These layers are connected by [NaO₆] octahedra that form chains along [100] (figure, top). The water molecules are located between [NaO₆] chains and at some apices of [CaO₆] and [NaO₆] polyhedra. Arsenic is coordinated with four oxygen atoms to form two crystallographically independent tetrahedra (As1 and As2). In

the [As(2)O₄] tetrahedra one of the oxygen atoms is attached to a hydrogen atom, thereby forming an acidic [HASO₄] group. Calcium is coordinated with six O atoms to form two crystallographically independent and irregular octahedra, [Ca(3)O₆] and [Ca(4)O₆]. The oxygen atom furthest from calcium in each octahedron belongs to a water molecule.

Table 1. Data collection and handling.

Crystal:	colorless, prismatic, size 0.03 × 0.10 × 0.13 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	60.51 cm ⁻¹
Diffractometer, scan mode:	Nonius CAD4, ω/2θ
2θ _{max} :	52.04°
N(hkl) _{measured} , N(hkl) _{unique} :	3802, 2538
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 1785
N(param) _{refined} :	149
Programs:	XABS2 [10], DIRDIF [11], SHELXL-97 [12], ATOMS [13], WinGX [14], ORTEP-II [15]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
O(7)	2i	0.0845(9)	0.3546(7)	0.3834(5)	0.029(1)
H(12A)	2i	0.3521	0.1145	0.2434	0.053
H(12B)	2i	0.1266	0.1680	0.2981	0.053
H(13)	2i	-0.0974	0.4352	0.2015	0.049
H(15A)	2i	0.4773	-0.2037	0.8484	0.069
H(15B)	2i	0.2948	-0.3414	0.8756	0.069
H(16A)	2i	0.2984	-0.1509	1.1952	0.069
H(16B)	2i	0.5302	-0.0834	1.1409	0.069
H(17A)	2i	0.4208	0.6800	0.2226	0.087
H(17B)	2i	0.6211	0.5635	0.2053	0.087
H(18A)	2i	0.1945	0.2118	0.9112	0.067
H(18B)	2i	0.0887	0.2707	1.0216	0.067
H(19A)	2i	0.2681	0.3861	0.1525	0.083
H(19B)	2i	0.2214	0.5549	0.0566	0.083

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
As(1)	2i	0.3303(1)	0.0069(1)	0.64055(8)	0.0272(4)	0.0102(4)	0.0361(4)	0.0147(2)	-0.0062(3)	-0.0031(3)
As(2)	2i	-0.0752(1)	0.5146(1)	0.34225(8)	0.0272(4)	0.0102(4)	0.0361(4)	0.0147(2)	-0.0062(3)	-0.0031(3)
Ca(3)	2i	0.3994(3)	0.3651(2)	0.4297(2)	0.0284(9)	0.0153(8)	0.041(1)	0.0168(6)	-0.0087(8)	-0.0069(8)
Ca(4)	2i	0.1433(2)	-0.1749(2)	0.4527(2)	0.0261(8)	0.0112(8)	0.039(1)	0.0139(6)	-0.0065(7)	-0.0037(7)
Na(6)	2i	0.2626(6)	-0.0458(5)	0.9542(4)	0.049(2)	0.029(2)	0.047(2)	0.019(2)	-0.011(2)	-0.009(2)
O(8)	2i	0.1865(8)	0.0315(6)	0.7640(5)	0.0272(4)	0.0102(4)	0.0361(4)	0.0147(2)	-0.0062(3)	-0.0031(3)
O(9)	2i	0.4969(9)	0.1656(7)	0.5879(6)	0.030(3)	0.015(3)	0.043(4)	0.014(2)	-0.007(3)	0.001(3)
O(10)	2i	0.1740(8)	0.0220(6)	0.5505(5)	0.0272(4)	0.0102(4)	0.0361(4)	0.0147(2)	-0.0062(3)	-0.0031(3)
O(11)	2i	0.7164(9)	0.4604(7)	0.4457(6)	0.030(3)	0.017(3)	0.040(4)	0.014(2)	-0.003(3)	-0.006(3)
O(12)	2i	0.211(1)	0.0717(8)	0.2817(6)	0.039(3)	0.020(3)	0.043(4)	0.016(3)	-0.009(3)	-0.006(3)
O(13)	2i	-0.1279(9)	0.5249(7)	0.2166(6)	0.036(3)	0.022(3)	0.036(4)	0.016(2)	-0.006(3)	-0.004(3)
O(14)	2i	0.0144(9)	-0.2975(7)	0.3385(6)	0.038(3)	0.009(3)	0.048(4)	0.014(2)	-0.008(3)	0.002(3)
O(15)	2i	0.3981(9)	-0.2976(5)	0.9093(4)	0.053(4)	0.031(4)	0.044(4)	0.019(3)	-0.006(3)	-0.001(3)
O(16)	2i	0.3920(8)	-0.0926(6)	1.1229(4)	0.059(4)	0.030(4)	0.045(4)	0.015(3)	-0.011(4)	-0.003(3)
O(17)	2i	0.473(1)	0.5612(8)	0.2399(4)	0.040(4)	0.039(4)	0.073(6)	0.023(3)	-0.005(4)	0.013(4)
O(18)	2i	0.0693(8)	0.1990(6)	0.9718(4)	0.051(4)	0.024(3)	0.053(5)	0.019(3)	-0.003(3)	-0.008(3)
O(19)	2i	0.203(1)	0.429(1)	0.0843(8)	0.061(5)	0.036(4)	0.055(5)	0.027(4)	-0.005(4)	-0.001(4)
O(21)	2i	0.4387(9)	-0.1819(7)	0.6775(6)	0.034(3)	0.011(3)	0.041(4)	0.016(2)	-0.010(3)	-0.002(3)

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