Crystal structure of dicalcium sodium monohydrogen diarsenate hexahydrate, $Ca_2Na[HAsO_4][AsO_4] \cdot 6H_2O$

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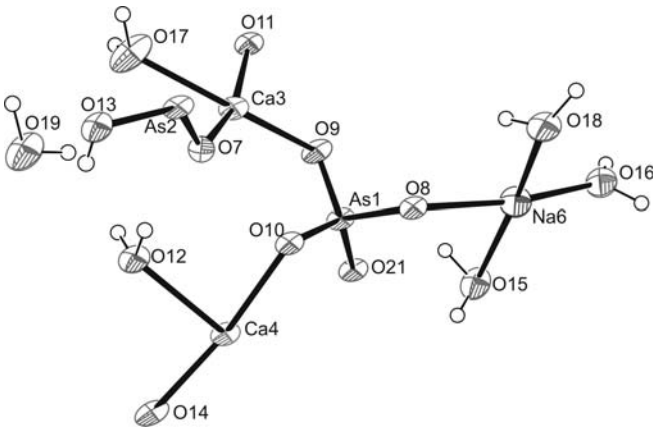

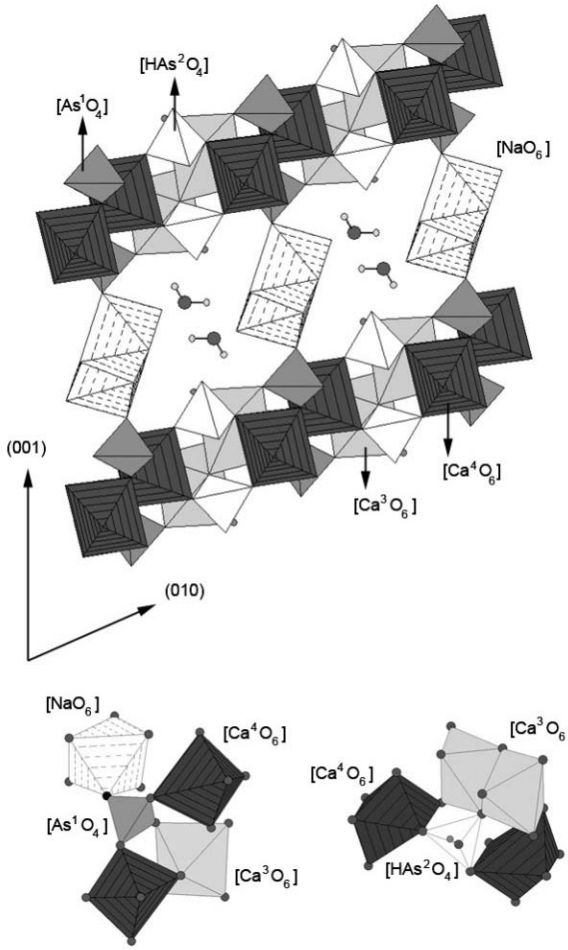

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Abstract

$As_2Ca_2H_{13}NaO_{14}$, triclinic, $P\bar{1}$ (no. 2), a = 6.680(5) Å, b = 8.223(4) Å, c = 12.537(3) Å, α = 73.46(5)°, β = 78.89(4)°, γ = 87.47(5)°, V = 647.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.062, $wR_{ref}(F^2)$ = 0.197, T = 293 K.

Source of material

Crystallization of $Ca_2Na(HAsO_4)(AsO_4) \cdot 6H_2O$ 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 cm^3 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 $Ca^{2+} + AsO_4^{3-}$ for $Na^+ + HAsO_4^{2-}$.

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 tobe 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 $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$ (guerinite and ferrarisite) and $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4H_2O$ (sainfeldite). Formation (at pH ca. 8) of guerinite, sainfeldite, and the new arsenate $NaCa_2(HAsO_4)(AsO_4) \cdot 6H_2O$ was observed in a previous study [9] on the interaction of As(V) with gypsum, which is the origin of the present work.

The crystal structure of $NaCa_2(HAsO_4)(AsO_4) \cdot 6H_2O$ is formed by (001) layers consisting of $[AsO_4]$ tetrahedra and $[CaO_6]$ polyhedra. These layers are connected by $[NaO_6]$ octahedra that form chains along [100] (figure, top). The water molecules are located between $[NaO_6]$ chains and at some apices of $[CaO_6]$ and $[NaO_6]$ polyhedra. Arsenic is coordinated with four oxygen atoms to form two crystallographically independent tetrahedra (As1 and As2). In the $[As(2)O_4]$ tetrahedra one of the oxygen atoms is attached to a hydrogen atom, thereby forming an acidic $[HAsO_4]$ group. Calcium is coordinated with six O atoms to form two crystallographically independent and irregular octahedra, $[Ca(3)O_6]$ and $[Ca(4)O_6]$. 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, $\omega/2\theta$
$2\theta_{max}$:	52.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3802, 2538
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 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 $Å^2$).

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

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	2*i*	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)	2*i*	–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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	–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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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)	2*i*	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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