Crystal structure of ammonium scandium diarsenate(V), $(\text{NH}_4)\text{ScAs}_2\text{O}_7$, the second KAIP_2O_7 -type diarsenate

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Abstract

$\text{As}_2\text{H}_4\text{NO}_7\text{Sc}$, monoclinic, $P12_1/c1$ (no. 14), $a = 7.842(2)$ Å, $b = 10.656(2)$ Å, $c = 8.765(2)$ Å, $\beta = 106.81(3)^\circ$, $V = 701.2$ Å³, $Z = 4$, $R(F) = 0.019$, $wR_{\text{ref}}(F^2) = 0.047$, $T = 293$ K.

Source of material

Prepared hydrothermally (493 K, 11 d) from a mixture of Sc_2O_3 , arsenic acid, ammonia and distilled water (final pH about 2; yield 100 %). The compound formed small, colorless pseudo-sphenoidal crystals.

Discussion

The present contribution is part of a recently started study on the crystal chemistry of Sc^{III} cations in oxysalts. Our first results led to the characterization of the crystallography and topology of four new alkali scandium arsenates synthesised by hydrothermal methods [1]. The title compound, $(\text{NH}_4)\text{ScAs}_2\text{O}_7$, is isotypic with KAIP_2O_7 [2], at least 27 other diphosphates (see [1] for details and discussion), and the diarsenate $\text{RbScAs}_2\text{O}_7$ [1], which is the only other KAIP_2O_7 -type diarsenate known.

The crystal structure contains one N, one Sc, two As, seven O and four H atoms, all of which occupy general positions. ScO_6 octahedra are corner-linked with As_2O_7 groups to form a three-dimensional, negatively charged framework in which six-sided tunnels parallel to $[001]$ are occupied by the charge-balancing

NH_4^+ cations. The irregular coordination environment of the NH_4^+ group consists of ten oxygen atoms within 3.5 Å, equivalent to the coordination of the Rb atom in the Rb analogue [1]. The NH_4^+ cations are linked to four of their closest oxygen neighbors via weak to very weak hydrogen-bonding, $d(\text{N} \cdots \text{O}) = 2.875(3)$ Å, $d(\text{N} \cdots \text{O}) = 2.896(3)$ Å, $d(\text{N} \cdots \text{O}) = 3.310(3)$ Å, $d(\text{N} \cdots \text{O}) = 2.951(3)$ Å. The ScO_6 octahedron is somewhat distorted, similar to the situation in $\text{RbScAs}_2\text{O}_7$ [1]. The average Sc—O bond length (2.088 Å) in the title compound is basically identical to that in $\text{RbScAs}_2\text{O}_7$ (2.090 Å). Both values are slightly smaller than the average value in oxidic Sc compounds (2.105 Å [3]). The average As—O bond lengths in the two non-equivalent AsO_4 tetrahedra [$d(\text{As1} \cdots \text{O}) = 1.679$ Å, $d(\text{As2} \cdots \text{O}) = 1.685$ Å] forming the As_2O_7 group are close to the expected value (1.682 Å [3]) and very close to those in $\text{RbScAs}_2\text{O}_7$ (1.681 Å and 1.684 Å, respectively [1]). The conformation of the As_2O_7 diarsenate group is nearly staggered, and is characterized by an $\text{As1} \cdots \text{O} \cdots \text{As2}$ angle of $120.09(9)^\circ$ (in $\text{RbScAs}_2\text{O}_7$ this angle is $119.62(10)^\circ$ [1], i.e., identical within error limits).

Bond-valence sums for all non-hydrogen atoms were calculated using the bond-valence parameters for Sc—O and As—O bonds from [4] and for NH_4 —O bonds from [5]. The sums obtained are 0.86 (NH_4), 5.10 (As1), 5.03 (As2), 3.16 (Sc), 2.07 (O1), 1.97 (O2), 2.07 (O3), 2.04 (O4), 1.95 (O5), 1.93 (O6), and 2.12 (O7) valence units (v.u.), and are thus all reasonably close to ideal valencies. A measured X-ray powder diffraction pattern (Cu K_α radiation) of the title compound shows good agreement with a calculated pattern.

Table 1. Data collection and handling.

Crystal:	colorless fragment, size $0.07 \times 0.08 \times 0.12$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	104.11 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, ϕ/ω
$2\theta_{\text{max}}$:	61°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4171, 2139
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2030
$N(\text{param})_{\text{refined}}$:	117
Programs:	SHELXS-97 [6], SHELXL-97 [7], ATOMS [8]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	1.109(6)	−0.868(4)	0.609(5)	0.04(1)
H(2)	4e	1.124(7)	−0.765(5)	0.505(6)	0.08(2)
H(3)	4e	1.22(1)	−0.872(7)	0.516(9)	0.13(3)
H(4)	4e	1.28(1)	−0.787(7)	0.613(9)	0.14(3)

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N	4e	1.1734(3)	−0.8227(3)	0.5531(3)	0.022(1)	0.033(1)	0.024(1)	−0.005(1)	0.0050(9)	0.002(1)
Sc	4e	0.76298(5)	−0.89894(3)	0.73795(4)	0.0089(2)	0.0080(2)	0.0103(2)	0.0003(1)	0.0029(1)	−0.0002(1)
As(1)	4e	0.86363(3)	−0.59201(2)	0.66835(2)	0.0107(1)	0.0100(1)	0.0094(1)	−0.00267(7)	0.00351(7)	−0.00053(7)
As(2)	4e	0.55738(3)	−0.86369(2)	0.30941(2)	0.0091(1)	0.0089(1)	0.0120(1)	−0.00080(7)	0.00341(7)	0.00083(7)
O(1)	4e	0.8533(3)	−0.9097(2)	0.9790(2)	0.032(1)	0.042(1)	0.0106(7)	0.0169(9)	0.0083(7)	0.0043(7)
O(2)	4e	0.6877(3)	−0.8900(2)	0.4914(2)	0.029(1)	0.034(1)	0.0110(7)	0.0043(8)	0.0002(7)	0.0050(7)
O(3)	4e	0.9988(2)	−0.9855(2)	0.7225(2)	0.0129(7)	0.0129(7)	0.0155(7)	0.0053(6)	0.0050(6)	0.0041(6)
O(4)	4e	0.9134(2)	−0.7331(2)	0.7513(2)	0.0141(7)	0.0089(7)	0.0250(8)	−0.0005(6)	0.0041(6)	0.0013(6)
O(5)	4e	0.6461(2)	−1.0771(2)	0.7250(2)	0.0108(7)	0.0131(7)	0.040(1)	−0.0044(6)	0.0094(7)	0.0005(7)
O(6)	4e	0.5454(2)	−0.7853(2)	0.7483(2)	0.0120(7)	0.0097(7)	0.0271(8)	0.0004(6)	0.0060(6)	−0.0045(6)
O(7)	4e	0.6532(2)	−0.9493(2)	0.1836(2)	0.0127(7)	0.0150(7)	0.0223(8)	−0.0020(6)	0.0070(6)	−0.0066(6)

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