

Alluaudite-Like Structure of the Arsenate $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$

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The arsenate $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ has been synthesized and investigated by X-ray diffraction and vibrational spectroscopy. According to a Rietveld analysis, it is monoclinic, space group $C2/c$, $Z = 4$, with $a = 12.6025$ (1), $b = 13.1699$ (1), $c = 6.8335$ (1) Å, $\beta = 113.7422$ (5). It has an alluaudite-like structure, with the three Na^+ cations located on the three large sites X(2), X(1), and M(1), and the two In^{3+} cations on the M(2) sites of this structure. This is a new type of chemical formula (free from bivalent cations and with a full occupancy of the X(2), X(1), and M(1) sites by sodium ions) for an alluaudite-like structure. The Raman and infrared spectra exhibit a great number of sharp bands, as expected from the low symmetry and from the ordered distribution of the cations, but this complexity precludes a detailed assignment of the bands. Structural analogies or differences with other alluaudite-like compounds are briefly discussed. © 1997

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INTRODUCTION

The structures of the arsenates $\text{Na}_3\text{M}_2^+(\text{AsO}_4)_3$ ($\text{M}^{3+} = \text{Al}, \text{Ga}, \text{Cr}, \text{Fe}, \text{Sc}$) are well known. On the contrary, no definite indexation has been proposed for the X-ray powder pattern of the corresponding indium compound $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ and, in fact, the existence of a definite compound corresponding to this nominal composition has not been proved beyond doubt (1). We show in this paper that $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ has an alluaudite-like structure. In fact, there is only one known arsenate mineral with the alluaudite structure (caryinite $\text{Na}(\text{Ca}, \text{Pb})_2(\text{Mn}, \text{Mg})_2(\text{AsO}_4)_3$ (2)). The first synthetic alluaudite arsenates have been reported in the doctoral thesis of Khorari (3) and the structure of some of them have been published recently (4–6).

EXPERIMENTAL

Synthesis of the compound. $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ can be synthesized, either by a conventional solid state reaction (starting from NaHCO_3 , In_2O_3 , and $\text{NH}_4\text{H}_2\text{AsO}_4$), or by a chemical attack of the reagents (NaHCO_3 , In_2O_3 , As_2O_3) by nitric acid, followed by evaporation to dryness. The dry mixture is slowly heated up to 650°C (one day), and then to

700°C (one day), and 800°C (one day) with intervening mixing and grinding. No attempt has been made to prepare single crystals.

X-ray diffraction. X-ray powder patterns were recorded with a Siemens D-5000 diffractometer ($\text{CuK}\alpha$ radiation; Si as the external standard). Unit cell parameters were refined with the INDLSQ least-square program. The alluaudite structure (strongly suggested by the successful indexation of the X-ray powder diagram) was definitely proved by a Rietveld analysis. The experimental details for the Rietveld refinement are given in Table 1.

Vibrational spectra. The IR spectra were recorded with a Beckman 4250 spectrometer ($2000\text{--}300\text{ cm}^{-1}$; KBr discs) and a Polytec FIR 30 interferometer ($350\text{--}30\text{ cm}^{-1}$; polyethylene discs). A spectrum was also run as a Nujol mull in order to check the lack of cationic exchange between the compound and the KBr disc. The Raman spectrum was recorded with a Coderg double monochromator equipped with an Ar^+ laser (laser power 200 mw on the 514.5 nm green line; spectral slit width about 1.5 cm^{-1}).

RESULTS

X-ray Diffraction

Indexation and unit cell parameters. An indexed X-ray powder pattern and the unit cell parameters are given in Table 2.

Rietveld refinement of the structure. Since all diffraction peaks are satisfactorily accounted for by a monoclinic cell, space group $C2/c$, and unit cell parameters similar to those of an alluaudite, this type of structure was considered for a Rietveld refinement, with the three relatively big Na^+ cations located on the three large cationic sites of the structure (namely X(2), X(1), and M(1)), and the two In^{3+} cations located on the two smaller octahedral sites M(2). The results are summarized in Tables 3 (positional and isotropic thermal parameters and site occupancy) and 4 (interatomic distances and angles).

The satisfactory values of R_p , R_{wp} , R_{exp} , GOF, and R_{Bragg} (Table 1) show that the alluaudite structure of Na_3In_2

(AsO₄)₃ can be considered as definitively proved. The geometry of the different cationic sites is represented in Fig. 1. This figure shows clearly the essential features of the structure: a very peculiar shape for X(2), a pseudo-cubic coordination of X(1), a very distorted octahedron for M(1), and a "classical" octahedron for M(2).

Vibrational Spectra

The vibrational spectra (Fig. 2) are essentially characterized by a large number of bands, their sharpness, and the occurrence of a sharp, isolated band at a relatively high frequency (in the 950–900 cm⁻¹ region).

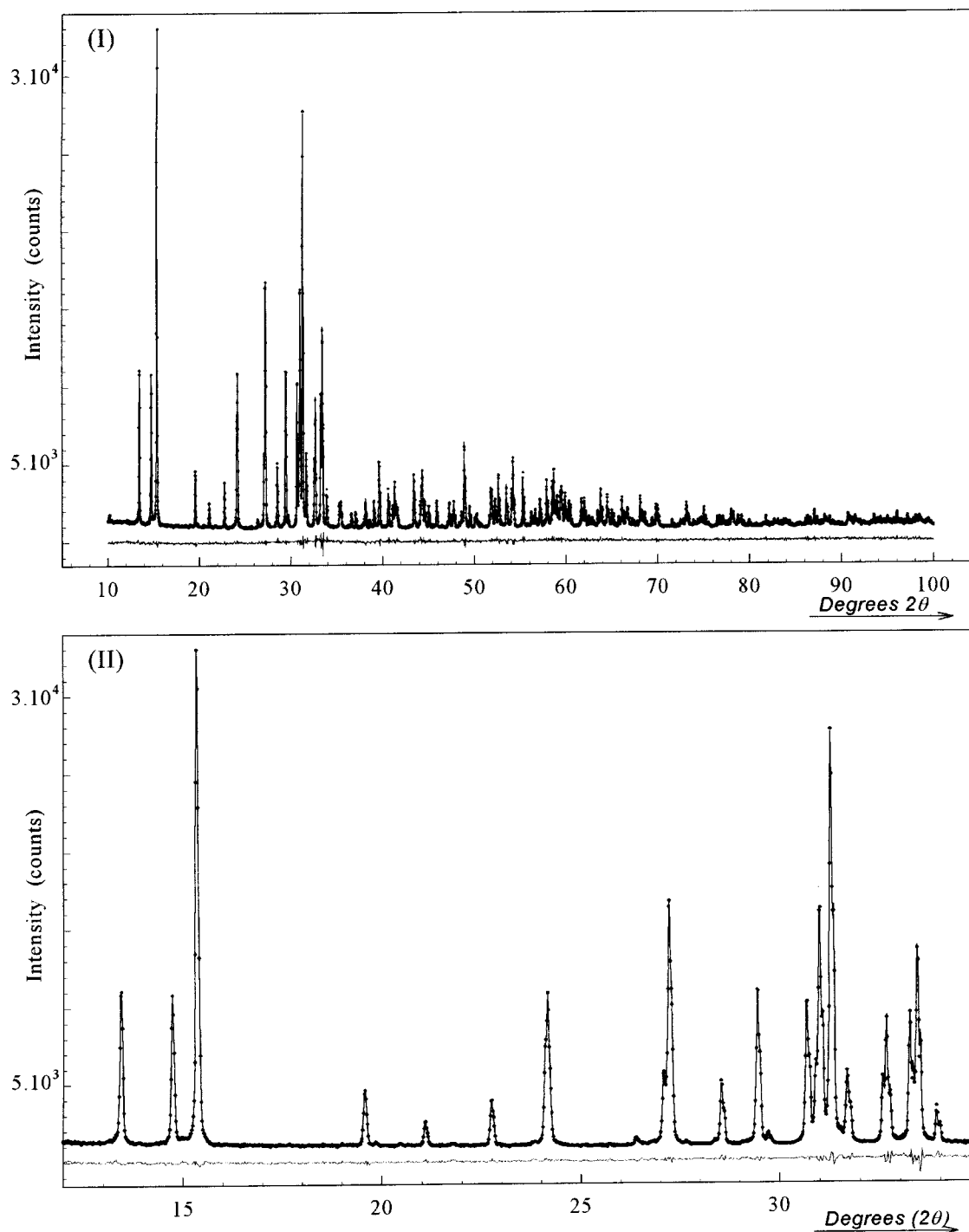


FIG. 1. (I) Final Rietveld plot for Na₃In₂(AsO₄)₃. Above, calculated (···) and observed (—) lines. The trace reported at the bottom is the plot of the difference (observed minus calculated). (II) Zoom between 12° and 35° (2θ).

TABLE 1
Experimental Details for the Rietveld Refinement

Diffractometer	Siemens D5000
Detector	PSD
Rietveld	R. A. Young (13)
2θ -range ($\text{CuK}\alpha$)	5–100
Step width ($^\circ 2\theta$ $\text{CuK}\alpha$)	0.02
Step time (s)	20
Number of reflections	1120
<i>Refined parameters</i>	
Structural parameters:	
positional	27
population	3
thermal (atomic displ.)	6
Cell parameters:	4
profile	5
Background	5
Zero-point (2θ)	1
Scale factor	1
Total	52
R_p (%)	4.21
R_{wp} (%)	5.63
$R_{(\text{Bragg})}$ (%)	5.02
GOF	2.16

This complexity is in agreement with the low symmetry of the structure and with the results of a factor group analysis (3, 4), according to which a total of 57 modes ($27 A_g + 30 B_g$) is expected in the Raman, and 60 modes ($29 A_u + 31 B_u$) in the IR spectrum (Table 5).

It is clear that a detailed assignment of such complex spectra is a hopeless task, not only because of the large number of active modes, but mainly because these modes are distributed over a small number of representations, thus allowing an extensive mixing of the vibrations which belong to the same representation. The following points are good examples of these difficulties:

(1) The high-frequency part ($950\text{--}750\text{ cm}^{-1}$) of the Raman spectrum of $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ exhibits 10 bands or shoulders (against a total of 12 expected fundamentals). These bands correspond to the stretching vibrations of the AsO_4 tetrahedra, but, apart from the specific case of the 934 cm^{-1} band, it is impossible to propose a more precise assignment to either $(\text{AsO}_4)(\text{I})$ or $(\text{AsO}_4)(\text{II})$ groups. In view of its high intensity and frequency, the 934 cm^{-1} band should be assigned to some A_g mode of the $(\text{AsO}_4)(\text{II})$ group, which is characterized by an abnormally short As–O bond (Table 4). For the remainder of the bands, we can just assume that the very strong band at 866 cm^{-1} is due to a ν_1 vibration, whereas the very weak ones are probably components issued from the split ν_3 vibrations.

The situation is still worse in the infrared spectrum, because of extensive overlapping of the bands. Here again,

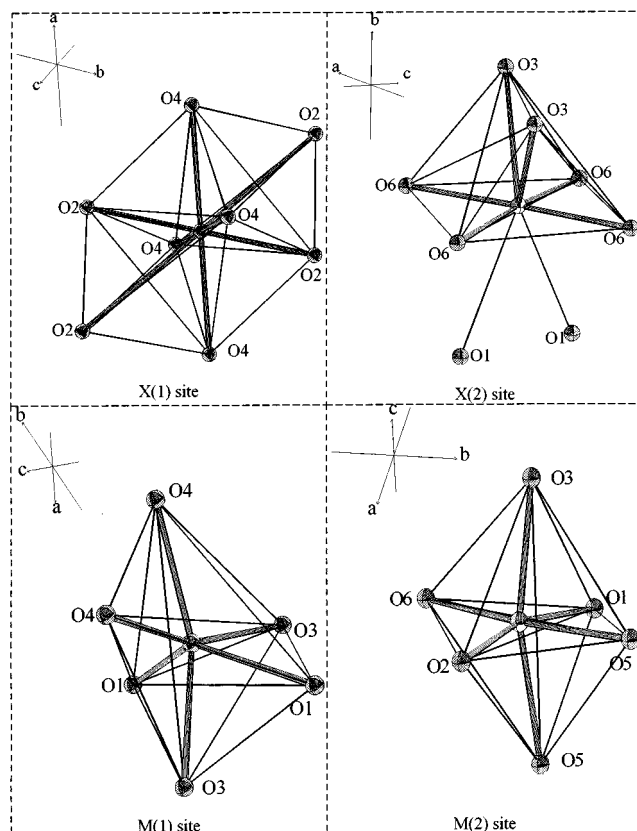


FIG. 2. Shape of the cationic sites X(1), X(2), M(1), and M(2).

the high-frequency (917 cm^{-1}) band should be correlated with the existence of a short As–O bond in the $(\text{AsO}_4)(\text{II})$ tetrahedron.

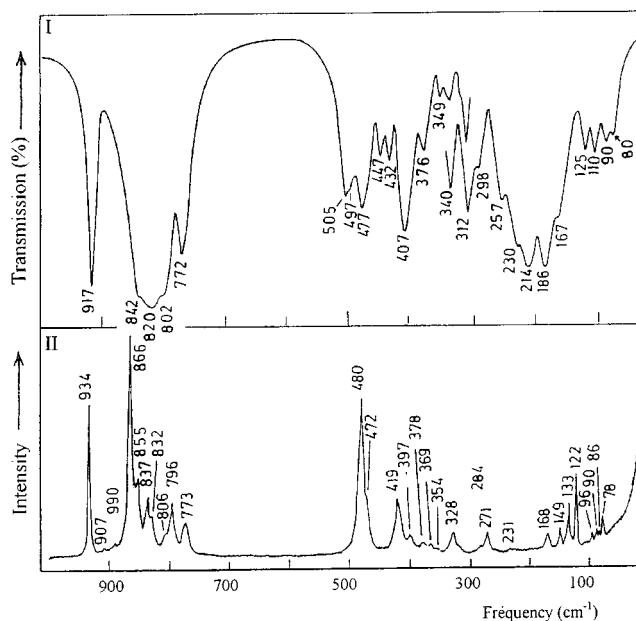


FIG. 3. Infrared (I) and Raman (II) spectrum of $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$.

TABLE 2
Indexed X-Ray Diagram of $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$, $K\alpha_2$ Filtered by Calculation

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (obs.)	<i>d</i> (cal.)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (obs.)	<i>d</i> (cal.)	<i>I</i> / <i>I</i> ₀
0	2	0	6.580700	6.583196	34	4	4	0	2.170500	2.169241	6
-1	1	1	5.998800	6.008803	30	-5	3	2	2.082500	2.082863	12
2	0	0	5.757600	5.768313	100	5	3	0	2.042800	2.042288	12
0	2	1	4.530100	4.534231	14	3	1	2	2.029000	2.030436	7
-2	2	1	4.211000	4.211085	9	-3	5	2	2.011200	2.011335	6
-3	1	1	3.906900	3.907270	11	-6	2	1	1.990900	1.991186	3
-1	3	1	3.681300	3.679935	30	-5	1	3	1.975400	1.974775	7
-2	0	2	3.375500	3.376536	5	3	5	1	1.921600	1.921463	7
-1	1	2	3.273700	3.274863	52	1	5	2	1.902800	1.902459	6
0	0	2	3.126200	3.127090	16	-2	4	3	1.872000	1.871418	6
-3	1	2	3.031900	3.032462	33	3	3	2	1.860500	1.861099	17
0	4	1	2.912400	2.912812	33	-2	6	2	1.839900	1.839967	6
4	0	0	2.884000	2.884156	49	-5	5	1	1.820000	1.820107	4
2	4	0	2.859300	2.858887	78	-1	7	1	1.812100	1.811943	4
-2	4	1	2.821500	2.821508	18	4	0	2	1.791800	1.791177	3
-4	0	2	2.739000	2.739282	23	0	4	3	1.761900	1.761207	9
1	1	2	2.693100	2.693395	30	1	7	1	1.748800	1.749041	7
-1	3	2	2.676900	2.678448	40	-6	4	2	1.737500	1.737542	11
4	2	0	2.641100	2.641751	10	4	2	2	1.727500	1.728346	4
-3	3	2	2.541200	2.540877	7	-3	5	3	1.711100	1.711053	9
-4	2	2	2.529700	2.529075	5	-2	0	4	1.691200	1.690560	14
-1	5	1	2.453600	2.453358	5	6	4	0	1.660400	1.660263	11
2	4	1	2.423100	2.423797	5	7	1	0	1.635000	1.635328	5
-2	4	2	2.357000	2.356968	7	-5	1	4	1.623200	1.623002	5
1	3	2	2.332000	2.331287	4	-3	7	2	1.610600	1.610318	7
1	5	1	2.302800	2.303609	8	-3	3	4	1.591600	1.591569	10
5	1	0	2.272600	2.272692	14	3	1	3	1.573800	1.573595	11
-3	1	3	2.218100	2.218830	10	1	7	2	1.553600	1.552792	10
0	6	0	2.194400	2.194398	7	1	7	2	1.553600	1.552792	9
-1	1	3	2.182200	2.182595	11						

$a = 12.601$ (1) Å
 $b = 13.166$ (1) Å
 $c = 6.8314$ (5) Å
 $\beta = 113.72$ (37)
 $V = 1037.66$ (9) Å³
 $F_{59} = 38.28$ (0.0100, 154)
 $M_{20} = 42.6$

Unit cell parameters deduced from the Rietveld refinement

$a = 12.6025$ (1) Å
 $b = 13.1699$ (1) Å
 $c = 6.83335$ (1) Å
 $\beta = 113.7422$ (5)

(2) Similar difficulties arise for the assignment of the ν_2 and ν_4 bending vibrations. The corresponding frequencies are observed at 342 (ν_2) and 398 (ν_4) in solution (7). Thus it is very probable that most of the bands of the 500–300 cm^{-1} region must be assigned to the bending vibrations of the AsO_4 tetrahedra, but it seems impossible to propose more precise assignments, namely a discrimination between $\text{AsO}_4(\text{I})$ and $\text{AsO}_4(\text{II})$ tetrahedra, or between ν_2 and ν_4 modes; moreover, such a discrimination is possibly insignificant (at least in part), because we do not know the amount of mixing which, according to the factor group analysis, is allowed between these vibrations (Table 5).

(3) The spectra exhibit, between 500 and 70 cm^{-1} , an uninterrupted series of bands, and there is no gap which could be interpreted as a separation between internal and

external modes. Thus, we can expect, in the 300 cm^{-1} region, an overlapping or even a mixing of the lowest AsO_4 bending frequencies and of the highest external frequencies, namely some of the In translational vibrations. The lowest-frequency bands are probably due, at least in part, to the translations of the weakly bonded Na^+ ions in the X(2) sites.

DISCUSSION

A New Type of Chemical Composition for the Alluaudite Structure

The presence of bivalent cations is a constant feature of all the alluaudite-like compounds reported so far. These cations can be either relatively large (such as Ca^{2+} or Cd^{2+}): they are located on the large sites of the alluaudite

TABLE 3
Positional and Isotropic Thermal Parameters and Site Occupancy

Site	Wyckoff	X	Y	Z	B (Å ²)	N
X(1) (Na)	4b	0	1/2	0	1.72(40)	1.004(9)
X(2) (Na)	4e	0	0.0047(8)	1/4	1.95(42)	0.991(9)
M(1) (Na)	4e	0	0.2742(8)	1/4	2.98(47)	1.043(9)
M(2) (In)	8f	0.2777(1)	0.6563(1)	0.3545(3)	0.48(4)	2 (fixed)
As(1)	4e	0	0.7228(3)	1/4	0.65(9)	1 (fixed)
As(2)	8f	0.2393(2)	0.8966(2)	0.1321(4)	0.56(6)	2 (fixed)
O(1)	8f	0.4540(10)	0.7014(9)	0.5338(18)	1 (fixed)	2 (fixed)
O(2)	8f	0.0975(9)	0.6409(8)	0.2244(17)	1 (fixed)	2 (fixed)
O(3)	8f	0.3344(9)	0.6673(9)	0.0949(17)	1 (fixed)	2 (fixed)
O(4)	8f	0.1258(9)	0.4201(8)	0.3195(17)	1 (fixed)	2 (fixed)
O(5)	8f	0.2325(9)	0.8233(8)	0.3297(17)	1 (fixed)	2 (fixed)
O(6)	8f	0.3408(8)	0.5027(8)	0.3842(15)	1 (fixed)	2 (fixed)

structure (X(2), X(1), and M(1)), or significantly smaller (Mg²⁺, Ni²⁺; located on the smallest M(2) sites), or with an intermediate size (Fe²⁺, Mn²⁺, located on either M(2) and M(1) sites).

Thus, Na₃In₂(AsO₄)₃ represents a new type of chemical composition for the alluaudite structure. In fact, it could be derived from the parent compound NaCa₂Mg₂(AsO₄)₃ by the coupled, charge-compensated substitution Ca₂²⁺Mg₂²⁺ → Na₂⁺In₂³⁺. It would be tempting to generalize this sub-

stitution by replacing In³⁺ by another trivalent cation M³⁺ (Fe, Cr, Ga). However, this generalization is not justified by the existing data, since the alluaudite structure of Na₃In₂(AsO₄)₃ is unique among the arsenates or phosphates Na₂M₂³⁺(AsO₄ or PO₄)₃ (see, e.g., (1) and references therein).

TABLE 5
Results of the Factor Group Analysis for Alluaudite-Like Na₃In₂(AsO₄)₃ (Space Group C2/c, C_{2h}⁶)

TABLE 4
Interatomic Distances (Å) and Angles (°)

X(2)–O(1) = 3.034(15) (× 2)	X(1)–O(2) = 2.405(11) (× 2)
X(2)–O(3) = 2.877(14) (× 2)	X(1)–O(2) = 3.219(11) (× 2)
X(2)–O(6) = 2.520(9) (× 2)	X(1)–O(4) = 2.366(11) (× 2)
X(2)–O(6) = 2.499(9) (× 2)	X(1)–O(4) = 2.591(10) (× 2)
Mean = 2.733	Mean = 2.645
M(1)–O(1) = 2.434(12) (× 2)	M(2)–O(1) = 2.144(12)
M(1)–O(3) = 2.383(13) (× 2)	M(2)–O(2) = 2.089(10)
M(1)–O(4) = 2.413(13) (× 2)	M(2)–O(3) = 2.168(11)
[M(1)–O(2) = 3.172(15) (× 2)]	M(2)–O(5) = 2.229(11)
Mean = 2.410	M(2)–O(5) = 2.262(11)
	M(2)–O(6) = 2.153(10)
	Mean = 2.174
As(1)–O(1) = 1.680(12) (× 2)	O(1)–As(1)–O(1) = 107.1(8)
As(1)–O(2) = 1.697(11) (× 2)	O(1)–As(1)–O(2) = 117.4(5) (× 2)
Mean = 1.689	O(1)–As(1)–O(2) = 107.2(5) (× 2)
	O(2)–As(1)–O(2) = 101.0(7)
	Mean = 109.6
As(2)–O(3) = 1.679(11)	O(3)–As(2)–O(4) = 115.3(2)
As(2)–O(4) = 1.626(11)	O(3)–As(2)–O(5) = 105.4(4)
As(2)–O(5) = 1.689(11)	O(3)–As(2)–O(6) = 105.0(5)
As(2)–O(6) = 1.701(10)	O(4)–As(2)–O(5) = 109.4(5)
Mean = 1.674	O(4)–As(2)–O(6) = 113.7(5)
	O(5)–As(2)–O(6) = 107.6(5)
	Mean = 109.4

	Wyckoff position	Site symmetry	Raman	Infrared
<i>Tetrahedral groups</i>				
<i>Internal modes</i>				
(AsO ₄)(1)	4e	C ₂	1 A _g	1 A _u
v ₁			2 A _g	2 A _u
v ₂			1 A _g + 2 B _g	1 A _u + 2 B _u
v ₃ or v ₄			1 A _g + 2 B _g	1 A _u + 2 B _u
Librations				
(AsO ₄)(2)	8f	C ₁	1 A _g + 1 B _g	1 A _u + 1 B _u
v ₁			2 A _g + 2 B _g	2 A _u + 2 B _u
v ₂			3 A _g + 3 B _g	3 A _u + 3 B _u
v ₃ or v ₄			3 A _g + 3 B _g	3 A _u + 3 B _u
Librations			3 A _g + 3 B _g	3 A _u + 3 B _u
<i>Translations</i>				
(AsO ₄)(1)	4e	C ₂	1 A _g + 2 B _g	1 A _u + 2 B _u
(AsO ₄)(2)	8f	C ₁	3 A _g + 3 B _g	3 A _u + 3 B _u
In	8f	C ₁	3 A _g + 3 B _g	3 A _u + 3 B _u
Na on M(1)	4e	C ₂	1 A _g + 2 B _g	1 A _u + 2 B _u
Na on X(1)	4b	C ₁	—	3 A _u + 3 B _u
Na on X(2)	4e	C ₂	1 A _g + 2 B _g	1 A _u + 2 B _u
<i>Total number of active modes</i>			<i>Raman</i>	<i>Infrared</i>
AsO ₄ stretching vibrations (v ₁ + v ₃)			12	12
AsO ₄ bending vibrations (v ₂ + v ₄)			15	15
Low-frequency vibrations (librations + translations)			30	33 ^a

^aAfter subtraction of the three acoustic modes.

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