Alluaudite-Like Structure of the Arsenate Na₃In₂(AsO₄)₃

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The arsenate Na₃In₂(AsO₄)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 In³⁺ 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 Academic Press

INTRODUCTION

The structures of the arsenates $Na_3M_2^{3+}(AsO_4)_3$ $(M^{3+} = Al, Ga, Cr, Fe, Sc)$ are well known. On the contrary, no definite indexation has been proposed for the X-ray powder pattern of the corresponding indium compound $Na_3In_2(AsO_4)_3$ 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 $Na_3In_2(AsO_4)_3$ has an alluaudite-like structure. In fact, there is only one known arsenate mineral with the alluaudite structure (caryinite $Na(Ca, Pb)_2(Mn, Mg)_2(AsO_4)_3$ (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. $Na_3In_2(AsO_4)_3$ can be synthesized, either by a conventional solid state reaction (starting from NaHCO₃, In_2O_3 , and $NH_4H_2AsO_4$), or by a chemical attack of the reagents (NaHCO₃, 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 (CuK α 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 (2000–300 cm⁻¹; KBr discs) and a Polytec FIR 30 interferometer (350–30 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 In³⁺ 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 $(AsO_4)_3$ 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 Na_3In_2 (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° (2 θ).

TABLE 1						
Experimental	Details for	the	Rietveld	Refinement		

Diffractometer	Siemens D5000
Detector	PSD
Rietveld	R. A. Young (13)
2θ -range (CuK α)	5-100
Step width (° 2θ CuK α)	0.02
Step time (s)	20
Number of reflections	1120
Refined parameters	
Structural parameters:	
positional	27
population	3
thermal (atomic displ.)	6
Cell parameters:	4
profile	5
Background	5
Zero-point (2θ)	1
Scle factor	1
Total	52
$R_{p}(\%)$	4.21
R _{wp} (%)	5.63
$R_{(Bragg)}(\%)$	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 $(950-750 \text{ cm}^{-1})$ of the Raman spectrum of Na₃In₂(AsO₄)₃ exhibits 10 bands or shoulders (against a total of 12 expected fundamentals). These bands correspond to the stretching vibrations of the AsO₄ tetrahedra, but, apart from the specific case of the 934 cm⁻¹ band, it is impossible to propose a more precise assignment to either (AsO₄)(I) or (AsO₄)(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 (AsO₄)(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 v_1 vibration, whereas the very weak ones are probably components issued from the split v_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 $(AsO_4)(II)$ tetrahedron.



FIG. 3. Infrared (I) and Raman (II) spectrum of Na₃In₂(AsO₄)₃.

 TABLE 2

 Indexed X-Ray Diagram of Na₃In₂(AsO₄)₃, Ka₂ Filtered by Calculation

h	k	l	<i>d</i> (obs.)	d(cal.)	I/I_0	h	k	l	<i>d</i> (obs.)	d(cal.)	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 b = 13.166 c = 6.8314 $\beta = 113.72$ V = 1037.6 $F_{59} = 38.22$	(1) Å (1) Å (5) Å (37) 56 (9) Å ³ 8 (0.0100), 154)			Unit cel a = 12.6 b = 13.1 c = 6.83 $\beta = 113$	l parameters dedu 025 (1) Å 699 (1) Å 335 (1) Å 7422 (5)	ced from	the Rietv	eld refinement		
10120 = 42.0	0										

(2) Similar difficulties arise for the assignment of the v_2 and v_4 bending vibrations. The corresponding frequencies are observed at $342 (v_2)$ and $398 (v_4)$ in solution (7). Thus it is very probable that most of the bands of the $500-300 \text{ cm}^{-1}$ region must be assigned to the bending vibrations of the AsO₄ tetrahedra, but it seems impossible to propose more precise assignments, namely a discrimination between AsO₄(I) and AsO₄(II) tetrahedra, or between v_2 and v_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 AsO₄ 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

Site	Wyckoff	X	Y	Z	B (Å ²)	Ν
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)

 TABLE 3

 Positional and Isotropic Thermal Parameters and Site Occupancy

structure (X(2), X(1), and M(1)), or significantly smaller $(Mg^{2+}, Ni^{2+}; located on the smallest M(2) sites)$, 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⁺ \rightarrow Na₂⁺In₂³⁺. It would be tempting to generalize this sub-

stitution by replacing In^{3+} by another trivalent cation M^{3+} (Fe, Cr, Ga). However, this generalization is not justified by the existing data, since the alluaudite structure of $Na_3In_2(AsO_4)_3$ is unique among the arsenates or phosphates $Na_2M_2^{3+}$ (AsO₄ or PO₄)₃ (see, e.g., (1) and references therein).

TABLE 5							
Results	of	the	Factor	Group	Analysis	for	Alluaudite-Like
	Ν	a ₃ In	12(AsO	4)3 (Spa	ce Group	C2	(c, C_{2h}^6)

Interatomic	TAI Distano	BLE 4 ces (Å) and Angles (°)			Wyckoff position	Site symmetry	Raman	Infrared
$\begin{array}{l} X(2)-O(1)=3.034(15)\\ X(2)-O(3)=2.877(14)\\ X(2)-O(6)=2.520(9)\\ X(2)-O(6)=\frac{2.499(9)}{Mean}\\ Mean=\frac{2.733}\\ M(1)-O(1)=2.434(12)\\ M(1)-O(3)=2.383(13)\\ M(1)-O(4)=2.413(13)\\ [M(1)-O(2)=\frac{3.172(15)}{Mean}\\ Mean=\frac{2.410}\\ \end{array}$	$(\times 2) \\ (\times 2)]$	$\begin{split} X(1)-O(2) &= 2.405(11) \\ X(1)-O(2) &= 3.219(11) \\ X(1)-O(4) &= 2.366(11) \\ X(1)-O(4) &= 2.591(10) \\ Mean &= 2.645 \\ \end{split}$ $\begin{split} M(2)-O(1) &= 2.144(12) \\ M(2)-O(2) &= 2.089(10) \\ M(2)-O(3) &= 2.168(11) \\ M(2)-O(5) &= 2.229(11) \\ M(2)-O(5) &= 2.262(11) \\ M(2)-O(6) &= 2.153(10) \\ \end{split}$	(×2) (×2) (×2) (×2)	Internal modes $(AsO_4)(1)$ v_1 v_2 v_3 or v_4 Librations $(AsO_4)(2)$ v_1 v_2 v_3 or v_4 Librations	Tet 4e 8f	trahedral grou C ₂ C ₁	$1 A_g$ $2 A_g$ $1 A_g + 2 B_g$ $1 A_g + 2 B_g$ $1 A_g + 1 B_g$ $2 A_g + 2 B_g$ $3 A_g + 3 B_g$ $3 A_g + 3 B_g$	$1 A_{u} 2 A_{u} 1 A_{u} + 2 B_{u} 1 A_{u} + 2 B_{u} 1 A_{u} + 2 B_{u} 1 A_{u} + 1 B_{u} 2 A_{u} + 2 B_{u} 3 A_{u} + 3 B_{u} 3 A_{u} + 3 B_{u} $
As(1)-O(1) = 1.680(12) As(1)-O(2) = 1.697(11) Mean = 1.689	(×2) (×2)	$\begin{array}{l} \text{M(a)} & 0.05 \\ \text{Mean} = 2.174 \\ \hline \\ \text{O(1)-As(1)-O(1)} = 107.1(8) \\ \text{O(1)-As(1)-O(2)} = 117.4(5) \\ \text{O(1)-As(1)-O(2)} = 107.2(5) \\ \text{O(2)-As(1)-O(2)} = \frac{101.0(7)}{109.6} \\ \hline \end{array}$	(×2) (×2)	(AsO ₄)(1) (AsO ₄)(2) In Na on M(1) Na on X(1) Na on X(2)	4e 8f 4e 4b 4e	$\begin{array}{c} Translations\\ C_2\\ C_1\\ C_1\\ C_2\\ C_i\\ C_2\\ C_1\end{array}$	$1 A_g + 2 B_g$ $3 A_g + 3 B_g$ $3 A_g + 3 B_g$ $1 A_g + 2 B_g$ $1 A_g + 2 B_g$	$\begin{array}{c} 1 \ A_{u} + 2 \ B_{u} \\ 3 \ A_{u} + 3 \ B_{u} \\ 3 \ A_{u} + 3 \ B_{u} \\ 1 \ A_{u} + 2 \ B_{u} \\ 3 \ A_{u} + 3 \ B_{u} \\ 1 \ A_{u} + 2 \ B_{u} \end{array}$
$\begin{array}{l} As(2)-O(3) = 1.679(11) \\ As(2)-O(4) = 1.626(11) \\ As(2)-O(5) = 1.689(11) \\ As(2)-O(6) = \underline{1.701(10)} \\ Mean = \overline{1.674} \end{array}$		$\begin{array}{l} O(3)-As(2)-O(4) = 115.3(2)\\ O(3)-As(2)-O(5) = 105.4(4)\\ O(3)-As(2)-O(6) = 105.0(5)\\ O(4)-As(2)-O(6) = 109.4(5)\\ O(4)-As(2)-O(6) = 113.7(5)\\ O(5)-As(2)-O(6) = 107.6(5)\\ Mean = \overline{109.4}\\ \end{array}$		Total number of AsO ₄ stretching vib AsO ₄ bending vib Low-frequency vib (librations + tran ^a After subtraction	active mode. brations $(v_1$ crations $(v_2 + v_1)$ rations nslations)	$(s + v_3)$ - v_4) ree acoustic m	<i>Raman</i> 12 15 30	Infrared 12 15 33 ^a

	NaCa ₂	$M_2^{2+}(AsO_4)_3^{a}$	NaM ₂ ³⁺ (AsO ₄) ₃	-
	M^{2+}		M ³⁺	
r	Ni Mg Co	Garnet	Cr Fe Garnet	
¥	 Mn	Alluaudite	In Alluaudite	

 TABLE 6

 Garnet versus Alluaudite Formation in Some Arsenates

"Synthesized by solid state reaction.

The corresponding phosphate $Na_3In_2(PO_4)_3$ is rhombohedral, with a Nasicon-like structure, but it is interesting to note that the arsenates $Na_3Cr_2(AsO_4)_3$ and Na_3Fe_2 $(AsO_4)_3$ have a garnet structure. This suggests a partial analogy with the crystallochemical behavior of the arsenates $NaCa_2M_2^{2^+}(AsO_4)_3$ ($M^{2^+} = Mg$, Ni, Co, Mn). If, in both families, we consider the cations (either M^{2^+} or M^{3^+}) arranged in the order of increasing ionic radii r_i (Table 6), we note that the small ones lead to a garnet structure, whereas the largest one (either Mn^{2^+} , or In^{3^+}) leads to an alluaudite structure. However, the analogy is not complete, since the high-temperature polymorph of the Cr^{3^+} and Fe^{3^+} has a rhombohedral (and not an alluaudite) structure.

Another point of interest is the full occupancy of the X(2), X(1), and M(1) sites by Na⁺ ions. This ion is a very common component of the alluaudite family and, in accordance with its relatively large ionic radius, it is known to go on the large sites of this structure. The study of the phosphate NaCdIn₂ (PO₄)₃ (8) shows that the Na⁺ ion is located entirely and exclusively on the X(1) site; but, in several other cases (e.g., NaCaCdMg₂(PO₄)₃, NaC₂M₂²⁺ (AsO₄)₃, NaCaCdMg₂ (AsO₄)₃), the distribution of the cations is partially disordered and no unique solution could be proposed for the structural role of Na⁺, which can be distributed over the three large sites of the alluaudite structure. In fact, Na₃In₂(AsO₄)₃ is the first reported example of the full occupancy in arsenates of the X(2) and M(1) sites by the Na⁺ cation.

Additional Comparisons with the Alluaudite Structure

Despite important differences in chemical composition, our results are in agreement with the descriptions of the alluaudite structure (and particularly of the important distorsion of the X(2), X(1), and M(1) sites) which have already been published, either for the mineral itself (9), or for synthetic compounds (5, 8, 10, 11).

Likewise, a comparison of some of the cation–oxygen distances in $NaCdIn_2(PO_4)_3$ (5) and $Na_3In_2(AsO_4)_3$ (this paper) shows similar values for the crystallographic sites which are occupied by the same cations in the two compounds, namely Na^+ on X(1), and In^{3+} on M(2) (Table 7).

 TABLE 7

 Comparison of Some Cation–Oxygen Distances in NaCdIn₂(PO₄)₃ and Na₃In₂(AsO₄)₃

X(1) (Na)-O(2) -O(4) -O(4) -O(2) Mean	NaCdIn ₂ (PO ₄) ₃ 2.34 2.37 2.66 $\frac{3.07}{2.61}$	$Na_{3}In_{2}(AsO_{4})_{3}$ 2.405 2.366 2.591 <u>3.219</u> <u>2.645</u>
M(2) (In)-O(6) -O(2) -O(1) -O(3) -O(5) -O(5) Mean	2.00 2.13 2.15 2.14 2.15 2.27 2.14	2.153 2.089 2.144 2.168 2.229 <u>2.262</u> 2.174

Some differences are observed for the individual distances (and this is not unexpected, since the distortion of the crystallographic sites is certainly not the same in the two compounds), but the mean values are very similar. The slightly larger values for $Na_3In_2(AsO_4)_3$ are possibly related to a small general expansion of the crystal cell due to the presence of an arsenate (against a phosphate) anion.

The main structural difference between $Na_3In_2(AsO_4)_3$ and the alluaudite-like compounds investigated so far lies in the type of cation distribution, which is fully ordered in the former compound and is partially disordered in most others.

The natural alluaudites are in fact solid solutions with a fairly complex composition, in which a partial disorder is clearly unavoidable. On the other hand, most of the synthetic compounds reported so far contain both Na⁺ and Ca²⁺ cations, whose ionic radii and electronic structures are very similar, thus leading to some disorder in the distribution of these cations over the large sites X(2), X(1), and M(1); e.g., NaCaCdMg₂(PO₄)₃ (10), NaCaCdMg₂(AsO₄)₃ (5) and NaCa₂M₂²⁺ (AsO₄)₃ (6). This disorder disappears in the case of the Ca-free phosphate NaCdIn₂(PO₄)₃, a defect structure with X(2) empty, Na⁺ on X(1) and Cd²⁺ on M(1) (8). Likewise, the replacement of Na⁺ by the larger K⁺ cation in NaCa₂Mg₂(AsO₄)₃ leads to an essentially order alluaudite KCa₂Mg₂(AsO₄)₃, because of the strong preference of the K⁺ cation for the large X(2) site (12).

As a consequence of these disorder phenomena, most of the published vibrational spectral are more or less diffuse (5, 4, 10, 12). On the contrary, sharp bands are observed in the spectra of $NaCdIn_2(PO_4)_3$ (8) and $Na_3In_2(AsO_4)_3$ (this paper).

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