Synthesis, crystal structure and charge-distribution validation of β-Na$_4$Cu(MoO$_4$)$_3$ adopting the alluadite structure-type

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Single crystals of a new variety of tetrasodium copper(II) tris[molybdate(VI)], Na$_4$Cu(MoO$_4$)$_3$, have been synthesized by solid-state reactions and characterized by single-crystal X-ray diffraction. This alluaudite structure-type is characterized by the presence of infinite layers of composition (Cu/Na)$_2$Mo$_3$O$_{14}$ parallel to the (100) plane, which are linked by MoO$_4$ tetrahedra, forming a three-dimensional framework containing two types of hexagonal channels in which Na$^+$ cations reside. The Cu^{2+} and Na^{2+} cations are located at the same general site with occupancies of 0.5. All atoms are on general positions except for one Mo, two Na (site symmetry 2) and another Na (site symmetry $\bar{1}$) atom. One O atom is split into two separate positions with occupancies of 0.5. The title compound is isotypic with Na$_5$Sc(MoO$_4$)$_4$ and Na$_3$In$_2$As$_3$O$_{12}$. The structure model is supported by bond-valence-sum (BVS) and charge-distribution CHARDI methods. β-Na$_4$Cu(MoO$_4$)$_3$ is compared and discussed with the K$_4$Cu(MoO$_4$)$_3$ and α-Na$_4$Cu(MoO$_4$)$_3$ structures.

1. Chemical context

In recent years, a number of molybdates have received considerable attention due to their amazing properties and high application potential in various fields, such as photoluminescence (Shi *et al.*, 2014) and Li-ion batteries (Reddy *et al.*, 2013). For example, the copper molybdate Cu$_3$Mo$_2$O$_9$ doped with lithium displays high Coulombic efficiency in lithium-ion batteries and excellent charge-discharge stability (Xia *et al.*, 2015). Many new molybdate phases have been synthesized and structurally characterized by X-ray diffraction, among which a large number belong to the alluaudite type, such as Na$_{25}$Cs$_8$Fe$_5$(MoO$_4$)$_{24}$, which presents a high electrical conductivity (Savina *et al.*, 2014). The alluaudite-type structure was first determined on natural minerals by Fisher, who showed that alluaudite compounds crystallize in the monoclinic $C2/c$ space group (Fisher, 1955). Moore proposed the general formula $X(2)X(1)M(1)M(2)_2$(PO$_4$)$_3$, in which the X and M mono-, bi- or trivalent cations are written according to their size (X are large cations and M are distorted octahedrally coordinated atoms). It represents the parental structure-type of the group referred to as alluaudite-type (Moore, 1971). The size of the channel and the stability of the alluaudite network led to many phases belonging to this structural type. We can totally or partially replace not only the monovalent cations, but also the central atoms of the MO$_6$ octahedra and TO$_4$ tetrahedra. It is also possible to make substitutions with cations in different oxidation states adopting the same type of coordination number (Mo^{6+}, V^{5+},
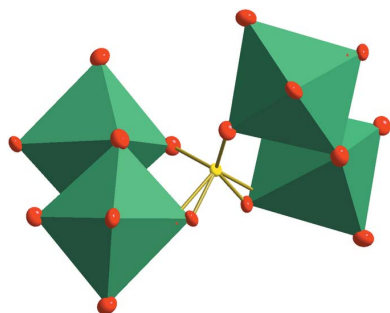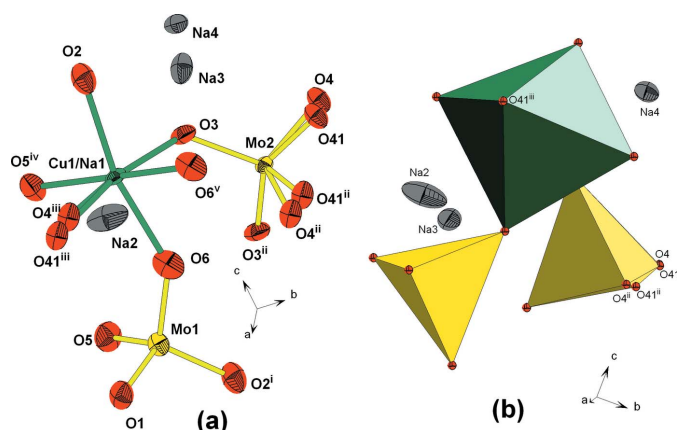
Figure 1
Representation of the coordination polyhedra in the structural unit of β-$Na_4Cu(MoO_4)_3$, showing (a) full atomic, (b) polyhedral. All atoms are represented as displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, -y, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.]

P^{5+} and As^{5+}). Alluaudite molybdates usually have the general formula of $X(2)X(1)M(1)M(2)_2(MoO_4)_3$ and adopt the $C2/c$ space group, with $a \simeq 12$, $b \simeq 13$ and $c \simeq 7$ Å, examples being the $K_{0.13}Na_{3.87}MgMo_3O_{12}$ (Ennajeh *et al.*, 2015), $Na_3Fe_2(MoO_4)_3$ (Muessig *et al.*, 2003) and $Na_4Co(MoO_4)_3$ (Nasri *et al.*, 2014) compounds. A review of the literature also reveals the presence of other formulae, such as

Table 1
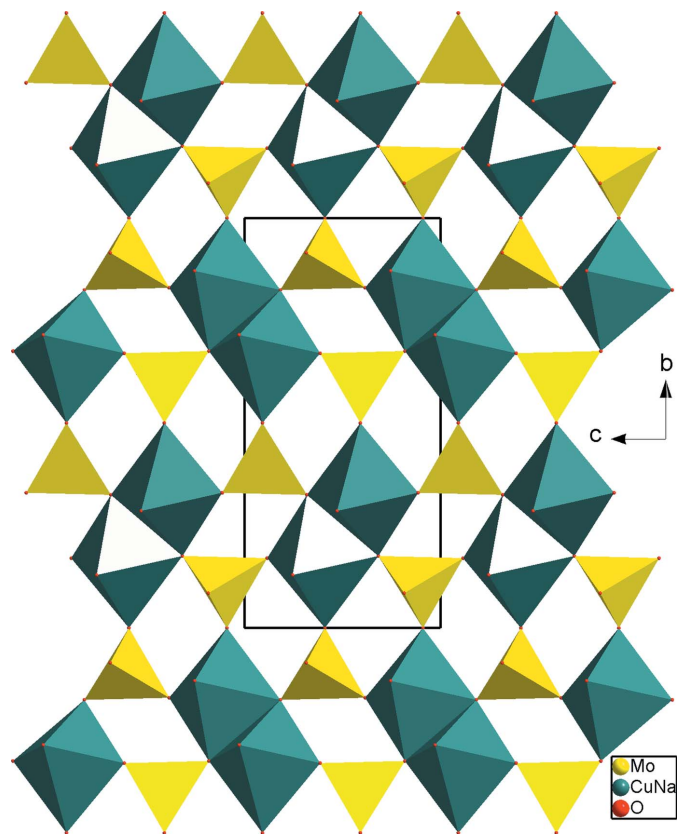Selected bond lengths (Å).

Mo1—O1	1.746 (3)	Na2—O5^{iv}	2.462 (3)
Mo1—O5	1.762 (3)	Na2—O5	2.549 (3)
Mo1—O2^{i}	1.764 (3)	Na2—O5^{ii}	2.549 (3)
Mo1—O6	1.774 (3)	Na3—O41^{vii}	2.443 (7)
Mo2—Mo2^{ii}	0.447 (2)	Na3—O41^{viii}	2.443 (7)
Mo2—O41	1.456 (7)	Na3—O1^{ix}	2.493 (3)
Mo2—O3^{ii}	1.738 (3)	Na3—O1^{ii}	2.493 (3)
Mo2—O41^{ii}	1.740 (7)	Na3—O1^{vi}	2.675 (3)
Mo2—O4	1.787 (7)	Na3—O1^{x}	2.675 (3)
Mo2—O3	1.822 (3)	Na3—O41^{vii}	2.749 (7)
Mo2—O4^{ii}	2.150 (6)	Na3—O4^{viii}	2.749 (7)
Cu1—O4^{iii}	1.884 (6)	Na3—O41^{xi}	3.008 (7)
Cu1—O3	2.098 (3)	Na3—O41^{xii}	3.008 (7)
Cu1—O2	2.116 (3)	Na4—O3	2.337 (2)
Cu1—O6	2.152 (3)	Na4—O3^{xiii}	2.337 (2)
Cu1—O5^{iv}	2.317 (3)	Na4—O2	2.424 (3)
Cu1—O6^{v}	2.464 (4)	Na4—O2^{xiii}	2.424 (3)
Cu1—O41^{iii}	2.467 (4)	Na4—O1^{v}	2.490 (4)
Na2—O5^{vi}	2.462 (3)	Na4—O1^{xiv}	2.490 (4)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, -y, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $-x + 1, -y, -z$; (vii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x - 1, -y, z - \frac{1}{2}$; (x) $x - 1, y, z$; (xi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (xii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (xiii) $-x + 1, y, -z + \frac{3}{2}$; (xiv) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

$Na_5Sc(MoO_4)_4$, $Na_2Ni(MoO_4)_2$ (Klevtsova *et al.*, 1991) and $Na_{2.2}Zn_{0.9}(MoO_4)_2$ (Efremov *et al.*, 1975), which crystallize in the space group $C2/c$ with cell parameters of about $a \simeq 12$, $b \simeq 13$ and $c \simeq 7$ Å. All alluaudite-type compounds can be described by the general formula given by Moore (1971), but their structures can differ by the number of formula units per unit cell. They are characterized by a three-dimensional heteropolyhedral framework formed by TO_4 tetrahedra and MO_6 octahedra, delimiting two types of channels running along the c axis. A new variety of β-$Na_4Cu(MoO_4)_3$ formulation was obtained by a reaction in the solid state at 873 K.

2. Structural commentary

The structural unit in β-$Na_4Cu(MoO_4)_3$ is formed by MO_6 (M = Cu1/Na1) octahedra linked by sharing vertices with $Mo1O_4$ tetrahedra and two slightly different $Mo2O_4$ tetrahedra, with a partially occupied (0.5 occupancy) Mo2 site. Atom O4 is split into two separate positions, with occupancies of 0.5 for the O4 and O41 atoms. The charge compensation is provided by Na^+ cations (Fig. 1). The essential building units of the structure are M_2O_{10} units obtained from two edge-sharing MO_6 octahedra. These units are connected by $Mo1O_4$ tetrahedra through vertex-sharing *via* Mo—O—M mixed bridges. This results in $M_2Mo_2O_{16}$ units. Each unit is connected to six other identical units by the sharing of vertices, leading to an infinite layer of the $M_2Mo_3O_{14}$ type parallel to the (100) plane (Fig. 2). The linkage of these layers is ensured by the two slightly different $Mo2O_4$ tetrahedra, linking *via* corners. This results in a three-dimensional framework delimited by two kinds of channels running along the c axis at $(\frac{1}{2}, 0, z)$ and $(0, 0, z)$. These channels are occupied by Na^+ cations (Fig. 3). In the anionic framework, each $Mo2O_4$ tetrahedron shares its O atoms with four different M_2O_{10} dimers belonging to two adjacent layers. The $Mo1O_4$ tetrahedron shares only three O

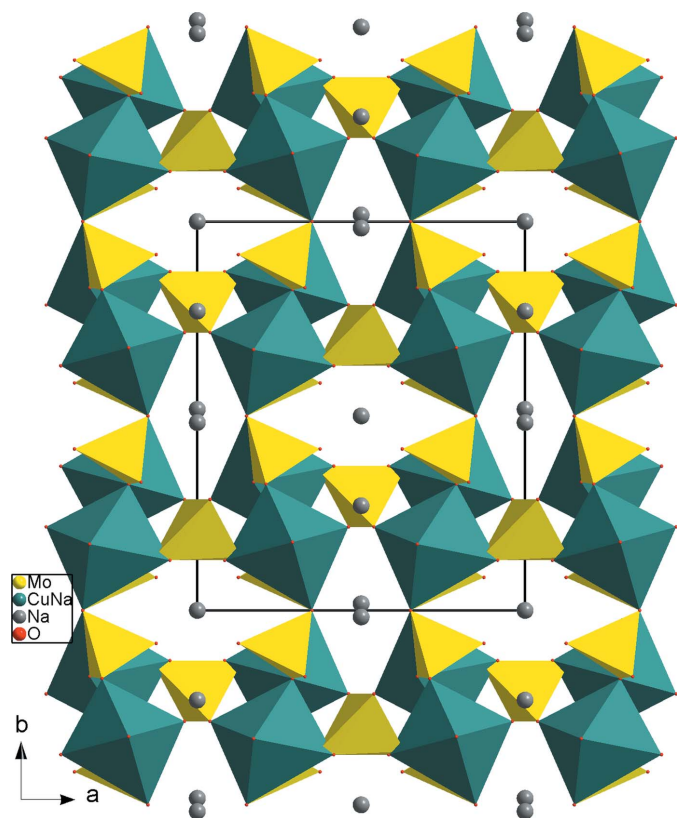**Figure 2**
A projection of the polyhedral layers in the bc plane.

Figure 3
A projection of the β-Na$_4$Cu(MoO$_4$)$_3$ structure, viewed normal to (001), showing the channels where monovalent cations are located.

atoms with three M_2O_{10} units belonging to the same layer, the other O atom being free and pointing towards the channels where the Na3 cations are located (Fig. 4). There is some compositional flexibility in the alluaudite structure and the studied material is isostructural with Na$_5$Sc(MoO$_4$)$_4$ (Klevt-sova *et al.*, 1975) and Na$_3$In$_2$As$_3$O$_{12}$ (Khorari *et al.*, 1997). The two crystallographically independent Mo atoms have tetrahedral coordination, with an average Mo—O distance of 1.761 Å for Mo1 and 1.777 Å for Mo2, which is in a good agreement with those typically observed in Rb$_2$Cu$_2$(MoO$_4$)$_3$
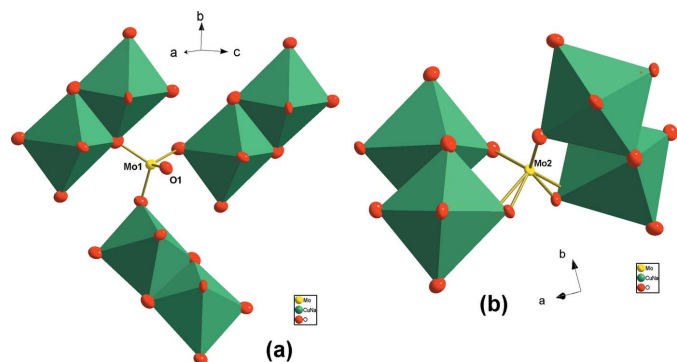

Figure 4
The association modes of M_2O_{10}-based units by the (*a*) Mo(1)O$_4$ and (*b*) Mo(2)O$_4$ tetrahedra. For clarity, we present only one atom of molybdenum, Mo2.

Table 2
CHARDI and BVS analysis of cation polyhedra in β-Na$_4$Cu(MoO$_4$)$_3$.

Cation	q(i)·sof(i)	Q(i)	V(i).sof(i)	CN(i)	ECoN(i)	d_{ar}	d_{med}
Mo1	6.00	6.24	5.93	4	4.00	1.761	1.761
Mo2	3.00	2.48	3.06	4	3.52	1.777	1.776
M	1.50	1.75	1.64	6	4.97	2.214	2.214
Na2	1.00	0.98	0.79	4	4.49	2.505	2.703
Na3	1.00	0.83	0.85	8	8.19	2.587	2.670
Na4	1.00	1.24	1.11	6	5.86	2.417	2.417

Notes: M = Cu1/Na1, q(i) = formal oxidation number, sof(i) = site-occupation factor, Q(i) = calculated charges, CN = coordination number, ECoN = number of effective coordination, MAPD = 100/NΣ_i^N.|qi - Qi/qi|, d_{ar} = arithmetic average distance and d_{med} = weighted average distance.

(Solodovnikov & Solodovnikova, 1997). The Na$^+$ cations occupy three crystallographically independent sites with different O-atom environments. The Na2, Na3 and Na4 atoms are surrounded by four, eight and six O atoms, respectively (Table 1). The Cu1 and Na1 cations are located at the same general site, with occupancies of 0.5, and have an octahedral environment with an average distance of 2.214 Å. This distance presents a mean between the Na—O distances of Na$_2$Cu(PO$_3$)$_4$ (Laügt *et al.*, 1972) and the Cu—O distances encountered in Ag$_2$Cu$_2$(MoO$_4$)$_3$ (Tsyrenova *et al.*, 2009). The proposed structural model is confirmed by two validation models: (i) the bond-valence approach using the empirical
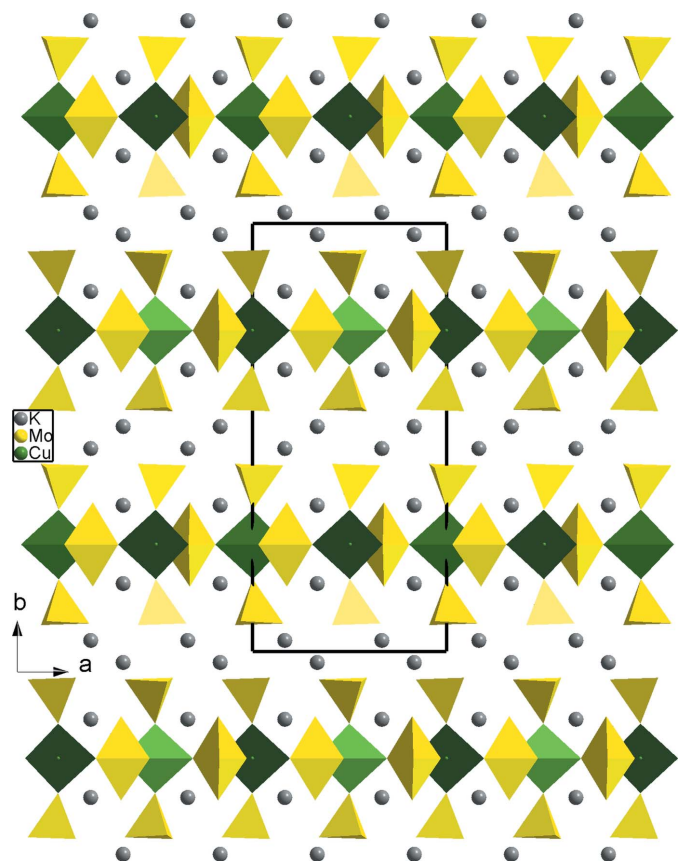

Figure 5
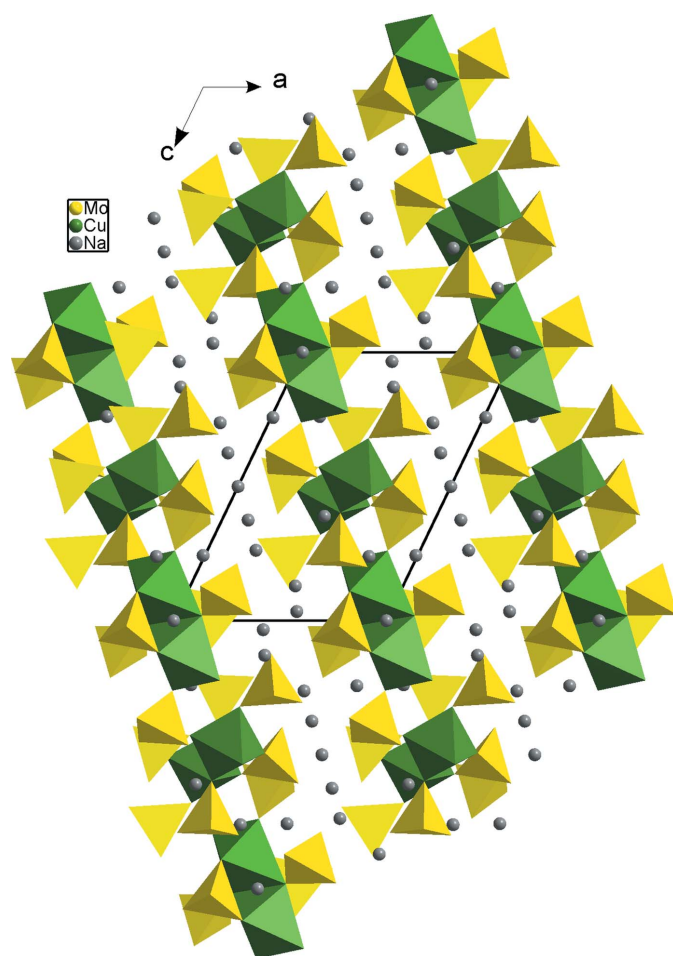A projection of the K$_4$Cu(MoO$_4$)$_3$ structure, viewed along the [001] direction.

Figure 6
A projection of the α-Na₄Cu(MoO₄)₃ structure, viewed in the (010) plane.

formula of Brown (Brown & Altermatt, 1985) and (ii) the charge-distribution method Chardi (Nespolo, 2015, 2016). The charge distribution method is the most recent development of Pauling's concept of bond strength (Pauling, 1929). Instead of empirical parameters used in the bond-valence approach, it exploits the experimental bond lengths deduced from the structural study to compute a non-integer coordination number, ECoN (effective coordination number), around a PC-atom (atom placed at the center of a polyhedron, $q > 0$), which is coordinated by V atoms (atoms located at the vertices, $q < 0$); q is the formal oxidation number. ECoN takes into account not only the number of V atoms around a given PC atom, but also their weight in terms of relative distances. Calculated charges $Q(i)$ and valences $V(i)$ are in good agreement with the formal oxidation number (q) multiplied by occupancy rates. The dispersion factor MAPD, which measures the mean absolute percentage deviation, is 2.2% for the calculated cationic charges. The variation of the ECoN value to the traditional coordination indicates the degree of distortion. The two validation models results are summarized in Table 2. Comparing our structure with that of a similar formulation, *i.e.* K₄Cu(MoO₄)₃ (Menard *et al.*, 2011), we found a clear difference, on the one hand, in the crystal symmetry and, on the other hand, in the arrangement of polyhedra. K₄Cu(MoO₄)₃

crystallizes in the *Pnma* space group. Its structure can be described as being composed of a distorted square-planar CuO₄ polyhedron bound by shared vertices to two Mo1O₄ tetrahedra to form CuMo₂O₁₀-type units. These units are interconnected, on the one hand, by insertion of two Mo2O₄ tetrahedra which share a face with a partial occupation (0.5 occupancy) of Mo2 atoms, and secondly by forming a mixed bridge of the Mo—O—Cu type. This forms ribbons arranged parallel to the [100] direction. This results in a one-dimensional structure in which K⁺ atoms reside in the inter-ribbon spaces (Fig. 5). The structure of our new variety β-Na₄Cu(MoO₄)₃ is compared with the α variety. Indeed, α-Na₄Cu(MoO₄)₃ (Klevtsova *et al.*, 1991) crystallizes in the triclinic system, space group $P\bar{1}$, and its structure is formed by the same Cu₂O₁₀ dimers present in our structure (here present as mixed-occupied M_2O_{10} units). The latter connects *via* Mo—O—Cu double composite bridges with two bidentate tetrahedra MoO₄ and by Mo—O—Cu simple bridges with monodentate MoO₄ tetrahedra to form Cu₂Mo₄O₂₀ units. The Cu₂Mo₄O₂₀ units are connected by MoO₄ tetrahedra and the pooling of vertices to form ribbons arranged in the [010] direction. All the ribbons form a one-dimensional framework with inter-ribbon spaces containing monovalent Na⁺ cations (Fig. 6). This structure has the same arrangement of structural units found in the one-dimensional structure of K₃Mn(MoO₄)₃ (Solodovnikov *et al.*, 1998) (Fig. 7).

3. Synthesis and crystallization

β-Na₄Cu(MoO₄)₃ crystals were obtained by a solid-state reaction from the following reagents: Na₂CO₃ (Prolabo, 70128), Cu(CO₂CH₃)·H₂O (Sigma–Aldrich, C5893) and (NH₄)₆Mo₇O₂₄·4H₂O (Sigma–Aldrich, 13301) with an Na:Cu:Mo molar ratio of 4:1:3. The resulting mixture was
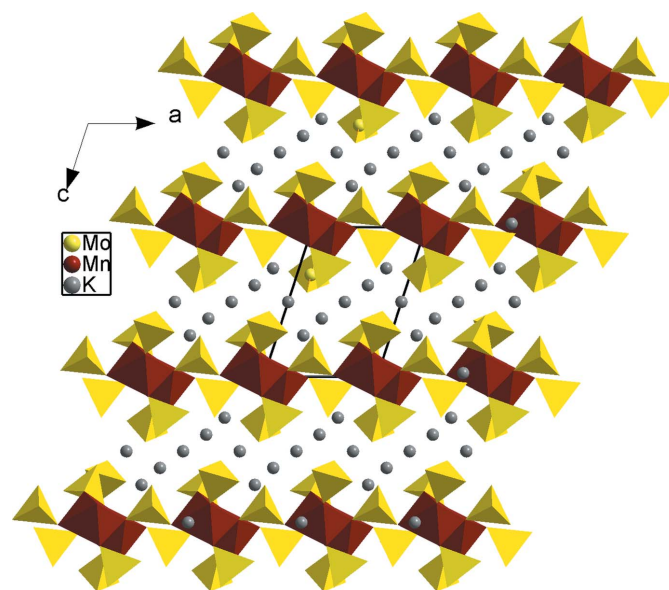
Figure 7
A projection of the K₄Mn(MoO₄)₃ structure, viewed normal to (010).

Table 3
Experimental details.

Crystal data	
Chemical formula	$Na_4Cu(MoO_4)_3$
M_r	635.32
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	298
a, b, c (Å)	12.5318 (9), 13.8181 (9), 7.1159 (7)
β (°)	111.95 (2)
V (Å^3)	1142.9 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.26
Crystal size (mm)	$0.28 \times 0.22 \times 0.18$
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.224, 0.387
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2678, 1238, 1208
R_{int}	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.058, 1.17
No. of reflections	1238
No. of parameters	104
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.80, −0.72

Computer programs: *CAD-4 EXPRESS* (Duisenberg, 1992), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 2001), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

milled in an agate mortar, placed in a porcelain crucible and then preheated slowly in air at 623 K for 24 h, in order to eliminate volatile products. Thereafter, it was heated to a temperature close to that of the fusion at 873 K. It was left at this temperature for 20 d to induce nucleation and crystal growth. The final residue was first cooled slowly (5 K per half day) to 823 K and then rapidly (50 K h^{-1}) to room temperature. Green crystals of sufficient size for the measurement of intensities were obtained.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. We used of EADP and EXYZ constraints within *SHELXL2014* (Sheldrick, 2015) for Cu1/Na1 located at the same crystallographic site. Atom O4 was split over two sites (O4 and O41) as this displayed a very elongated displacement ellipsoid. The occupancies of O4 and O41 were set to 0.5 in line with the occupany of Mo2; the two separate O-atom sites (O4 and O41) correspond to two different orientations of the Mo2O4 tetrahedron related by symmetry. Refining atomic occupancies leads to a value of 0.497 (4) for the Cu atom. For conditions of electrical neutrality, we set the occupancy of the Cu atom as 0.5. This

leads to well-defined ellipsoids. The maximum and minimum electron densities in the final Fourier difference map are acceptable and located at 0.77 and 0.82 Å, respectively, from the Na2 and Mo1 atoms.

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supporting information

Synthesis, crystal structure and charge-distribution validation of *β*-Na₄Cu(MoO₄)₃ adopting the alluadite structure-type

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Computing details

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992); cell refinement: *CAD-4 EXPRESS* (Duisenberg, 1992); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Tetrasodium copper(II) tris[molybdate(VI)]

Crystal data

$Na_4Cu(MoO_4)_3$	$F(000) = 1180$
$M_r = 635.32$	$D_x = 3.692$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.5318\,(9)$ Å	Cell parameters from 25 reflections
$b = 13.8181\,(9)$ Å	$\theta = 10–15°$
$c = 7.1159\,(7)$ Å	$\mu = 5.26$ mm^{-1}
$\beta = 111.95\,(2)°$	$T = 298$ K
$V = 1142.9\,(2)$ Å^3	Prism, green
$Z = 4$	$0.28 \times 0.22 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1238 independent reflections
	1208 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.030$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{max} = 27.0°$, $\theta_{min} = 2.3°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.224$, $T_{max} = 0.387$	$k = -1 \rightarrow 17$
2678 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 5.2182P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.058$	$\Delta\rho_{max} = 0.80$ e Å^{-3}
$S = 1.17$	$\Delta\rho_{min} = -0.72$ e Å^{-3}
1238 reflections	Extinction correction: SHELXL2014 (Sheldrick, 2015),
104 parameters	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
0 restraints	Extinction coefficient: 0.00081 (11)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mo1	0.72812 (2)	0.10879 (2)	0.11920 (4)	0.01991 (12)	
Mo2	0.48085 (7)	0.28610 (4)	0.2400 (3)	0.0133 (3)	0.5
Cu1	0.70643 (5)	0.16100 (5)	0.61691 (9)	0.01741 (16)	0.5
Na1	0.70643 (5)	0.16100 (5)	0.61691 (9)	0.01741 (16)	0.5
Na2	0.5000	0.0169 (3)	0.2500	0.0482 (8)	
Na3	0.0000	0.0000	0.0000	0.0299 (5)	
Na4	0.5000	0.26934 (16)	0.7500	0.0219 (4)	
O1	0.8745 (2)	0.0849 (2)	0.1859 (4)	0.0292 (6)	
O2	0.6715 (2)	0.1702 (2)	0.8852 (4)	0.0337 (6)	
O3	0.5390 (2)	0.2147 (2)	0.4714 (4)	0.0247 (6)	
O4	0.3657 (5)	0.3629 (6)	0.2376 (11)	0.0239 (10)	0.5
O41	0.4153 (5)	0.3707 (6)	0.2551 (11)	0.0239 (10)	0.5
O5	0.6504 (3)	−0.0001 (2)	0.0904 (5)	0.0346 (7)	
O6	0.7095 (3)	0.1754 (2)	0.3178 (5)	0.0373 (7)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01593 (17)	0.02069 (18)	0.01973 (18)	0.00034 (10)	0.00275 (11)	−0.00104 (11)
Mo2	0.0147 (8)	0.0162 (2)	0.0079 (4)	0.0004 (2)	0.0032 (6)	0.0000 (3)
Cu1	0.0227 (3)	0.0219 (3)	0.0093 (3)	−0.0007 (3)	0.0079 (2)	0.0006 (2)
Na1	0.0227 (3)	0.0219 (3)	0.0093 (3)	−0.0007 (3)	0.0079 (2)	0.0006 (2)
Na2	0.0217 (11)	0.098 (3)	0.0203 (11)	0.000	0.0031 (9)	0.000
Na3	0.0397 (12)	0.0224 (10)	0.0179 (9)	−0.0013 (10)	−0.0004 (9)	−0.0006 (9)
Na4	0.0225 (9)	0.0270 (11)	0.0189 (9)	0.000	0.0110 (7)	0.000
O1	0.0187 (12)	0.0341 (15)	0.0307 (14)	0.0037 (11)	0.0044 (10)	0.0072 (12)
O2	0.0268 (14)	0.0330 (16)	0.0327 (15)	0.0083 (12)	0.0011 (12)	0.0017 (13)
O3	0.0275 (13)	0.0335 (15)	0.0160 (12)	−0.0003 (12)	0.0113 (10)	0.0011 (11)
O4	0.017 (3)	0.0250 (18)	0.0238 (18)	0.005 (3)	0.001 (3)	−0.0039 (16)
O41	0.017 (3)	0.0250 (18)	0.0238 (18)	0.005 (3)	0.001 (3)	−0.0039 (16)
O5	0.0357 (15)	0.0279 (14)	0.0410 (17)	−0.0059 (13)	0.0152 (13)	0.0005 (13)
O6	0.0305 (14)	0.0398 (17)	0.0385 (17)	0.0010 (14)	0.0095 (13)	−0.0084 (14)

Geometric parameters (Å, º)

Mo1—O1	1.746 (3)	Na2—O5[iv]	2.462 (3)
Mo1—O5	1.762 (3)	Na2—O5	2.549 (3)
Mo1—O2[i]	1.764 (3)	Na2—O5[ii]	2.549 (3)
Mo1—O6	1.774 (3)	Na3—O41[vii]	2.443 (7)

Mo2—Mo2ⁱⁱ	0.447 (2)	Na3—O41ᵛⁱⁱⁱ	2.443 (7)
Mo2—O41	1.456 (7)	Na3—O1ⁱˣ	2.493 (3)
Mo2—O3ⁱⁱ	1.738 (3)	Na3—O1ⁱⁱ	2.493 (3)
Mo2—O41ⁱⁱ	1.740 (7)	Na3—O1ᵛⁱ	2.675 (3)
Mo2—O4	1.787 (7)	Na3—O1ˣ	2.675 (3)
Mo2—O3	1.822 (3)	Na3—O4ᵛⁱⁱ	2.749 (7)
Mo2—O4ⁱⁱ	2.150 (6)	Na3—O4ᵛⁱⁱⁱ	2.749 (7)
Cu1—O4ⁱⁱⁱ	1.884 (6)	Na3—O41ˣⁱ	3.008 (7)
Cu1—O3	2.098 (3)	Na3—O41ˣⁱⁱ	3.008 (7)
Cu1—O2	2.116 (3)	Na4—O3	2.337 (2)
Cu1—O6	2.152 (3)	Na4—O3ˣⁱⁱⁱ	2.337 (2)
Cu1—O5ⁱᵛ	2.317 (3)	Na4—O2	2.424 (3)
Cu1—O6ᵛ	2.464 (4)	Na4—O2ˣⁱⁱⁱ	2.424 (3)
Cu1—O41ⁱⁱⁱ	2.467 (4)	Na4—O1ᵛ	2.490 (4)
Na2—O5ᵛⁱ	2.462 (3)	Na4—O1ˣⁱᵛ	2.490 (4)
O1—Mo1—O5	110.42 (15)	O3—Cu1—O2	85.28 (10)
O1—Mo1—O2ⁱ	111.01 (14)	O4ⁱⁱⁱ—Cu1—O6	93.4 (2)
O5—Mo1—O2ⁱ	106.95 (15)	O3—Cu1—O6	82.16 (11)
O1—Mo1—O6	108.63 (14)	O2—Cu1—O6	166.61 (12)
O5—Mo1—O6	107.69 (15)	O4ⁱⁱⁱ—Cu1—O5ⁱᵛ	96.1 (2)
O2ⁱ—Mo1—O6	112.08 (15)	O3—Cu1—O5ⁱᵛ	94.73 (11)
O3ⁱⁱ—Mo2—O4	118.4 (2)	O2—Cu1—O5ⁱᵛ	88.43 (12)
O3ⁱⁱ—Mo2—O3	110.75 (17)	O6—Cu1—O5ⁱᵛ	97.18 (12)
O4—Mo2—O3	112.3 (3)	O6ᵛ—Cu1—O2	89.55 (14)
O3ⁱⁱ—Mo2—O4ⁱⁱ	100.3 (2)	O6ᵛ—Cu1—O4ⁱⁱⁱ	76.78 (15)
O4—Mo2—O4ⁱⁱ	113.9 (4)	O6ᵛ—Cu1—O5ⁱᵛ	172.13 (15)
O3—Mo2—O4ⁱⁱ	99.0 (2)	O6ᵛ—Cu1—O6	86.42 (14)
O4ⁱⁱⁱ—Cu1—O3	168.8 (2)	O6ᵛ—Cu1—O3	92.66 (12)
O4ⁱⁱⁱ—Cu1—O2	98.1 (2)		

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1, y, -z+1/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x, -y, z+1/2$; (v) $-x+3/2, -y+1/2, -z+1$; (vi) $-x+1, -y, -z$; (vii) $x-1/2, -y+1/2, z-1/2$; (viii) $-x+1/2, y-1/2, -z+1/2$; (ix) $x-1, -y, z-1/2$; (x) $x-1, y, z$; (xi) $-x+1/2, -y+1/2, -z$; (xii) $x-1/2, y-1/2, z$; (xiii) $-x+1, y, -z+3/2$; (xiv) $x-1/2, -y+1/2, z+1/2$.