

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K. M., Al-Laham, A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. & Pople, J. A. (1995). *GAUSSIAN94*. Revision E.3. Gaussian Inc., Pittsburgh, PA, USA.
- Fu, W. T., de Gelder, R. & de Graaff, R. A. G. (1997). *Mater. Res. Bull.* **32**, 657–662.
- Ijdo, D. J. W. & Helmholdt, R. B. (1993). *Acta Cryst.* **C49**, 652–654.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- McDowell, R. S. & Asprey, C. B. (1972). *J. Chem. Phys.* **57**, 3062–3068.
- Milne, J. B. & Moffett, D. (1973). *Inorg. Chem.* **12**, 2240–2244.
- Monconduit, L., Tillard, M., Favier, F. & Belin, C. (1999). *J. Alloys Compd.* Submitted.
- Moritani, T., Kuchitsu, K. & Morino, Y. (1971). *Inorg. Chem.* **10**, 344–350.
- Pauling, L. (1947). *J. Am. Chem. Soc.* **69**, 542–543.
- Pauling, L. (1949). *Proc. R. Soc. London*, **A196**, 343–354.
- Shao, M., Jin, X., Tang, Y., Huang, Q. & Huang, Y. (1982). *Tetrahedron Lett.* **23**, 5343–5347.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sportouch, S., Belin, C. & Tillard-Charbonnel, M. (1994). *Acta Cryst.* **C50**, 1861–1862.

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The lamellar double-hydroxide (LDH) compound with composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$

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Abstract

The title compound, tetracalcium dialuminum dodecahydroxide dinitrate tetrahydrate, of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$, is a layered compound constituted by positively charged $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{2+}$ main layers and negatively charged $[2\text{NO}_3\cdot 4\text{H}_2\text{O}]^{2-}$ interlayers. It crystallizes in the trigonal $P\bar{3}c1$ space group. The interlayer part of the structure is strongly disordered.

The Al^{3+} and Ca^{2+} ions are six- and seven-oxygen-coordinated, respectively. Half of the water molecules and nitrate groups assume statistically the seventh coordination position of the calcium ions. Thus, half the water molecules are considered as bonded water and half as free or slightly bonded. The planar NO_3^- groups are bonded and perpendicular to the main layers. Nitrate groups are on disordered positions close to the [001] axis and free water molecules fill the interlayer space, also in a disordered manner. This is interpreted as a dynamic disorder resulting from free rotation of the nitrate group around the [001] axis, and this interpretation is compatible with Raman microspectroscopy results realised on the same specimen used for this study.

Comment

The title compound, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$, and several of the many related basic salts called AFm phases are important because they occur on hydration of cements. They form positively charged brucite-like $[\text{Ca}_2(\text{Al},\text{Fe})(\text{OH})_6]^+$ layers and negatively charged $[\text{X}_z\cdot n\text{H}_2\text{O}]^-$ interlayers to assume electroneutrality; X is a monovalent anion $[\text{OH}^-, \text{Cl}^-, \text{NO}_3^-, \text{Al}(\text{OH})_4^-]$ with $z = 1$ or a bivalent anion $(\text{CO}_3^{2-}, \text{SO}_4^{2-})$ with $z = \frac{1}{2}$, where n can vary depending on the humidity, the temperature and the nature of the inserted anion. A structural model for these AFm phases has been proposed but not refined (Ahmed & Taylor, 1967). At present, structures based on single-crystal data have been determined for the monosulfate $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ (Allmann, 1977) and the chloride $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ (Terzis *et al.*, 1987). Recently, the equivalent carbonated compound $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ was studied. Two modifications of this phase were resolved. The first is totally ordered (François *et al.*, 1998), whereas the interlayer region of the second presents a statistical disorder between one carbonate group and three water molecules (Renaudin *et al.*, 1999).

The chemical composition of the compound $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$, commonly named binitroaluminat, was checked by a thermogravimetric experiment, taking into account the indications given by Ahmed *et al.* (1968) on its thermal decomposition. The studied compound crystallizes in the centrosymmetric trigonal space group $P\bar{3}c1$. Hexagonal parameters are consistent with those previously indicated (Kuzel, 1970). The structure contains nine crystallographic non-H atom sites. There is one $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$ formula unit per lattice. Selected interatomic distances are reported in Table 2. The main layers of the structure defined by Al, Ca and O sites are completely ordered, while the interlayers, filled by water molecules (OW1 and OW2) and nitrate groups (ON1, N, ON2 and ON3), are disordered, as seen by occupancy factors inferior to the unity and elevated displacement parameters.

A general view of the structure projected along the [110] direction is shown in Fig. 1. This representation has been ordered for clarity on the (3*a*, 3*b*, 2*c*) lattice. It can be described by the stacking sequence of planes (NO₃⁻, H₂O)–[Ca₄Al₂(OH)₁₂]²⁺–(NO₃⁻, H₂O)–2H₂O *etc.*, parallel to (001). Two adjacent [Ca₄Al₂(OH)₁₂]²⁺ main layers are separated by a distance of 8.62 Å. This distance is 7.55 Å in the equivalent carbonated compound; the difference of ≈1.1 Å is explained by the different orientations of the planar anionic NO₃⁻ and CO₃²⁻ groups. While the carbonate groups tend to be parallel to the main layers [tilted by 21.8 (3)^o], the nitrate groups are perpendicular to these layers. The oxygen environment of the Ca²⁺ and Al³⁺ cations are represented in Fig. 2. The coordination number is 6 and 7 for the Al³⁺ and Ca²⁺ cations, respectively. The seventh coordination position of the Ca atoms is assumed statistically either by OW1 water molecules or by nitrate ON1 atoms. The two possibilities are shown in Fig. 2.

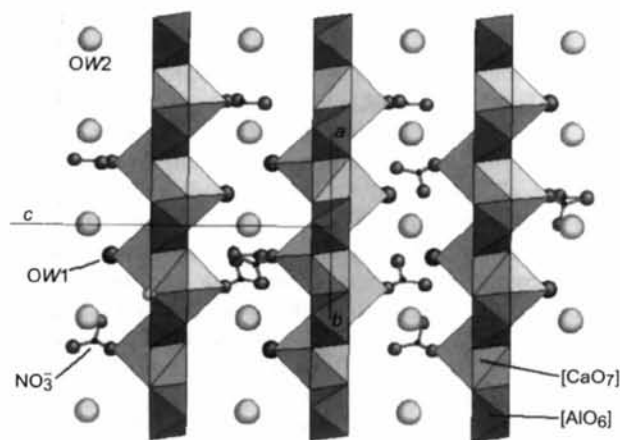


Fig. 1. Projection of the layered structure of 3CaO·Al₂O₃·Ca(NO₃)₂·10H₂O along [110]. The [AlO₆] and [CaO₇] polyhedra were produced using *CaRIne* (Boudias & Monceau, 1997). The interlayer part of the structure is represented in an ordered way for clarity, *i.e.* disordered OW2 free water molecules are fixed on special position (0,0, $\frac{1}{4}$). NO₃⁻ groups are drawn in a definite orientation and the choice between one OW1 bonded water molecule or one nitrate anion is organized.

A dynamic disorder of the nitrate group and the free water OW2 molecule exists. This is shown by the elevated displacement parameters of the considered atoms and the Raman microspectroscopy results from the same single crystal. It is interpreted as a free rotation of NO₃⁻ and the free OW2 water molecule around the *c* axis, as it was supposed but not proven in an earlier work (Ahmed *et al.*, 1968). The various positions of the nitrate group around the ternary axis are represented in Fig. 3. The Raman spectrum in the range 3450–3850 cm⁻¹ relating hydroxyl vibrations did not show any well defined hydrogen bonds, but did show a large distribution of them, in agreement with

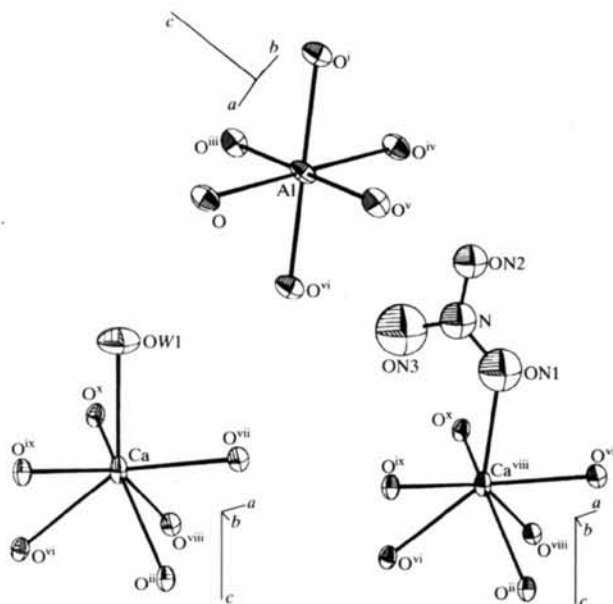


Fig. 2. The oxygen environment of the Al³⁺ and Ca²⁺ cations within the [Ca₄Al₂(OH)₁₂]²⁺ main layers. The two possible Ca²⁺ environments are drawn (with OW1 bonded water or nitrate group bonded *via* ON1). Displacement ellipsoids are drawn at the 50% probability level (*ATOMS*; Dowty, 1995). Symmetry codes: (i) $-y, x-y, z$; (ii) $x-y, x, -z$; (iii) $y-x, -x, z$; (iv) $-x, -y, -z$; (v) $x-y, x, -z$; (vi) $y, 1+y-x, -z$; (vii) $1-x+y, 1-x, z$; (viii) $1-x, 1-y, -z$; (ix) $1-y, x-y, z$; (x) $x, 1+y, z$.

a dynamic disorder. In order to assume distances above 2.4 Å between the nitrate ON3 atom and the free OW2 water molecule, the latter had to be shifted from the special position (0,0, $\frac{1}{4}$) to a general position. Thus, the positions of the nitrate groups and free OW2 water molecules are closely linked. Because of the great disorder in the interlayer part of the structure, the H atoms of the two water molecules (bonded OW1 and free OW2) could not be localized.

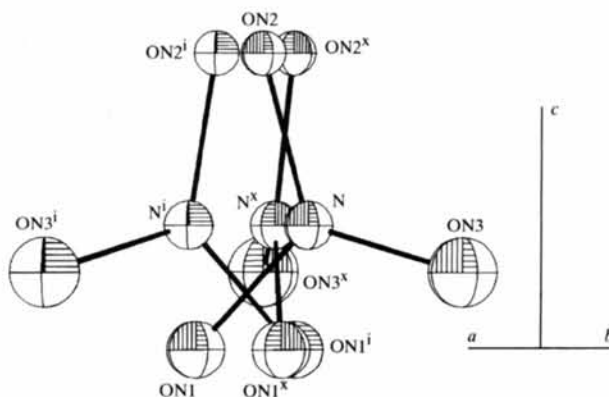


Fig. 3. View of the [2NO₃·4H₂O]²⁻ interlayers showing the disorder in that part of the structure. The representation is partially ordered, as indicated in the text. Isotropic displacement ellipsoids are drawn at the 10% probability level (*ATOMS*; Dowty, 1995).

Experimental

The single crystal of the title compound used for analysis was prepared by hydrothermal synthesis. The starting powders Ca(OH)₂, Al(OH)₃ and Ca(NO₃)₂·4H₂O in the stoichiometric proportion 3/2/1 were mixed with water (ratio solid:water = 0.5), loaded into a silver capsule (length 100 mm, diameter 5 mm, thickness 0.1 mm) and sealed under an argon atmosphere. The experiment was performed over a period of two months at a temperature of 393 K and a pressure of 2 Kbar (1 bar = 10⁵ Pa).

Crystal data

[Ca₄Al₂(OH)₁₂](NO₃)₂·4H₂O Mo K α radiation
M_r = 614.46 λ = 0.71073 Å
 Trigonal Cell parameters from 25 reflections
*P*3̄*c*1 θ = 7–11°
a = 5.7445 (8) Å μ = 1.296 mm⁻¹
c = 17.235 (5) Å *T* = 293 (2) K
V = 492.55 (16) Å³ Plate
Z = 1 0.320 × 0.200 × 0.075 mm
D_x = 2.072 Mg m⁻³ Colourless
D_m not measured

Data collection

Enraf–Nonius CAD-4 416 reflections with
 diffractometer *I* > 2σ(*I*)
 $\omega/2\theta$ scans *R*_{int} = 0.017
 Absorption correction: θ_{\max} = 29.92°
 empirical fitted by *h* = 0 → 6
 spherical harmonic *k* = 0 → 6
 functions (SORTAV; *l* = 0 → 24
 Blessing, 1995) 3 standard reflections
*T*_{min} = 0.666, *T*_{max} = 0.909 frequency: 180 min
 2025 measured reflections intensity decay: 5.9%
 522 independent reflections

Refinement

Refinement on *F*² $w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.5390P]$
 $R[F^2 > 2\sigma(F^2)] = 0.036$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.100$ $(\Delta/\sigma)_{\max} = 0.004$
 $S = 1.164$ $\Delta\rho_{\max} = 0.442 \text{ e } \text{Å}^{-3}$
 455 reflections $\Delta\rho_{\min} = -0.627 \text{ e } \text{Å}^{-3}$
 41 parameters Extinction correction: none
 H atoms treated by a mixture of independent and constrained refinement Scattering factors from *International Tables for Crystallography* (Vol. C)

ON2‡	0.394 (3)	0.680 (5)	0.2965 (6)	0.044 (3)
ON3‡	0.619 (5)	0.974 (4)	0.2061 (11)	0.106 (8)
OW2‡	1.045 (9)	0.908 (6)	0.264 (2)	0.128 (14)

† Site occupancy = 0.50. ‡ Site occupancy = 0.1667.

Table 2. Selected bond distances (Å)

Al—O	1.9082 (14)	Ca—ON1	2.46 (2)
Ca—O ⁱ	2.3609 (16)	Ca—OW1	2.466 (9)
Ca—O ⁱⁱ	2.4485 (15)		

Symmetry codes: (i) -y, x - y, z; (ii) x - y, x, -z.

The title structure was refined in the centrosymmetric space group *P*3̄*c*1, with an *R* value of 0.036. An attempt to refine the structure in the non-centrosymmetric space group *P*3*c*1 did not decrease the disorder observed in the interlayer region. Refinement of the main layers leads to an *R* value of 0.080, with Al atoms on the 2*b* site, Ca atoms on the 4*d* site, hydroxyl groups on general position 12*g* and the seven Ca²⁺-coordinated O atoms on special position 4*d*. These four atoms were refined with anisotropic displacement parameters. Hydroxyl H atoms were located from difference Fourier maps and refined with fixed individual isotropic displacement parameters [*U*_{iso} = 1.2*U*_{eq}(O)], using a riding model with an O—H distance of 0.95 (2) Å. The positions of the interlayer atoms were found from difference Fourier maps. An attempt to place nitrate groups parallel to the main layers was not conclusive. In agreement with the 8.6 Å layer thickness, nitrate groups were placed perpendicular to the main layers. NO₃⁻ groups are bonded to Ca²⁺, so 50% of the Ca atoms are linked to a water molecule and the other 50% are linked to a nitrate group via the ON1 atom placed on the same site as OW1 in a first run. Nitrate-group geometry (sites ON1, ON2, ON3 and N) was restrained to be flat, with an O—N—O angle of 120°, and N—ON1, N—ON2 and N—ON3 distances identical within an s.u. of 0.02 Å. The free water molecule (OW2) was localized from difference Fourier maps on special site 2*a*. This model leads to an *R* value of 0.07. Continuation of the refinement consists of displacing the interlayer nitrate group and free water molecule from their special positions. Thus, the ON1, ON2, ON3, N and OW2 atoms were placed on general site 12*g* (keeping the same restraints on the nitrate group). The refinement of this second kind of disorder, interpreted as free rotation of nitrate and affecting also the free water molecule (OW2) position, is in agreement with the large isotropic displacement parameters of these atoms and the Raman spectroscopy observations on the same single crystal, and leads to a residual *R* value of 0.036.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREAR* (Blessing, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *ATOMS* (Dowty, 1995) and *CaRine* (Boudias & Monceau, 1997). Software used to prepare material for publication: *WINWORD* (Version 5.0).

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Al	0	0	0	0.0129 (3)
Ca	1/3	2/3	0.03345 (4)	0.0165 (2)
O	0.3070 (3)	0.0572 (3)	0.05807 (8)	0.0169 (3)
OW1†	1/3	2/3	0.1765 (5)	0.047 (3)
ON1‡	0.287 (5)	0.579 (4)	0.1741 (12)	0.072 (7)
N‡	0.428 (3)	0.745 (3)	0.2254 (7)	0.052 (4)

The authors are grateful to the Service Commun de Diffractométrie Automatique of the University Henri Poincaré and to Alain Rouiller from CRPG for his help in the preparation of the hydrothermal syntheses.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1257). Services for accessing these data are described at the back of the journal.

Comment

Franzen *et al.* (1972) reported the preparation, crystal structure and physical properties of a triclinic phase of sodium tungsten oxide with a stoichiometry corresponding to the formula Na₆W₁₄O₄₅. The synthesis was achieved by electrolyzing fused mixtures of Na₂WO₄ and WO₃ of compositions used to prepare the well known tetragonal sodium tungsten bronze and at temperatures just above the melting point of the solution. At higher temperatures, the tetragonal sodium tungsten bronze phase was obtained. The single-crystal X-ray diffraction study revealed the positions of the W atoms, while the positions of the Na and O atoms could not be located due to the poor quality of the crystals obtained. However, Franzen *et al.* (1972) were able to propose a model for the structure based solely on the derived positions of the W atoms. Since there appeared to be considerable difficulty in relating the measured electrical properties of the studied phase with its structure, it was considered worthwhile to carry out a new structure investigation. The phase is pseudo-monoclinic, with a C-lattice type and cell constants, calculated from the reduced ones (LEPAGE; Spek, 1988), of $a = 12.672(2)$, $b = 7.274(1)$, $c = 18.551(3)$ Å, $\alpha = 89.29(1)$, $\beta = 97.75(1)$ and $\gamma = 90.27(1)^\circ$. These values are comparable with the corresponding values calculated from the data given by Franzen *et al.* (1972) of $a = 12.577$, $b = 7.287$, $c = 18.474$ Å, $\alpha = 89.40$, $\beta = 95.66$ and $\gamma = 89.40^\circ$.

There are three Na, seven W and 22 O atoms in the asymmetric unit of the structure, all lying in general positions, except for Na1 which lies on a symmetry centre. The present study confirmed the existence in the structure of groups of four layers, which consist of WO₆ octahedra sharing their corners in the *ab* plane. These layers are of the type found in the hexagonal bronzes, *e.g.* in Rb_{0.27}WO₃ (Magnéli, 1953), but of different stacking mode. While in the hexagonal bronzes the layers are superimposed along *c*, leading to tunnels of trigonal and hexagonal sections, in the structure of Na₅W₁₄O₄₄, the layers are displaced relative to each other, so that some WO₆ octahedra of a certain layer project onto the hexagonal holes of a lower one, thus hindering the formation of tunnels. The first layer in such a group comprises the metal atoms Na2, W2, W3 and W4 ($z = 0.16$ – 0.19 ; Fig. 1*a*). Similarly, the second layer comprises the metal atoms Na3, W5, W6 and W7 ($z = 0.37$ – 0.40 ; Fig. 1*b*). The third and fourth layers are derived from the second and first ones, respectively, *via* inversion through a symmetry centre with $z = \frac{1}{2}$. All the WO₆ octahedra are considerably distorted, the observed W–O distance range being 1.68(2)–2.39(2) Å. Such a range is not unexpected, *e.g.* in Na₂W₄O₁₃, it is 1.71(2)–2.28(5) Å (Viswanathan, 1974). There is also a fifth layer in the structure, comprising the metal atoms Na1 and W1 ($z = 0$ – 0.03 ; Fig. 1*c*), of a completely

References

- Ahmed, S. J., Dent-Glasser, L. S. & Taylor, H. F. W. (1968). 5th Symp. Chem. Cem. pp. 118–127, Supplementary Paper II-77.
 Ahmed, S. J. & Taylor, H. F. W. (1967). *Nature*, **215**, 622–623.
 Allmann, R. (1977). *Neues Jahrb. Mineral. Monatsh.* **3**, 136–144.
 Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Boudias, C. & Monceau, D. (1997). *CaRIne Crystallography*. Version 3.1. Distributed by Divergent SA, Rond Point Guy Denielou, Centre de Transfert, 60200 Compiègne, France.
 Dowty, E. (1995). *ATOMS for Windows*. Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 François, M., Renaudin, G. & Evrard, O. (1998). *Acta Cryst.* **C54**, 1214–1217.
 Kuzel, H. J. (1970). *Neues Jahrb. Mineral. Monatsh.* pp. 363–374.
 Renaudin, G., François, M. & Evrard, O. (1999). *Cem. Conc. Res.* **29**, 63–69.
 Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Terzis, A., Filippakis, S., Kuzel, H.-J. & Burzlaff, H. (1987). *Z. Kristallogr.* **181**, 29–34.

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Triclinic sodium tungsten oxide, Na₅W₁₄O₄₄

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Abstract

The structure of the title compound, pentasodium tetradecatungsten tetratetracontaoxide, is built up of groups of four layers of WO₆ octahedra similar to those found in the hexagonal tungsten bronzes, but displaced relative to each other so that no tunnels of trigonal and hexagonal sections are formed. These groups are linked together through a layer of a different type consisting of isolated WO₅ trigonal bipyramids. The Na atoms are distributed in the hexagonal holes of the above layers, being coordinated in all cases by eight O atoms in a hexagonal bipyramidal arrangement.