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Octacaesium Decatungstosilicate Nonahydrate

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Abstract

The title compound {octacaesium silicodecatungstate nonahydrate, $\text{Cs}_8[\text{SiW}_{10}\text{O}_{36}]\cdot 9\text{H}_2\text{O}$ } is the first caesium salt of the heteropolyoxometalate anion $\gamma\text{-}[\text{SiW}_{10}\text{O}_{36}]^{8-}$. The stability of the well known heteropolyanion depends on the size of the alkali metal cations. The polyanions are connected into infinite columns by Cs cations.

Comment

Heteropolytungstates have been known for a long time and are interesting for many reasons (Pope & Müller, 1991; Lunk, 1990). Polyanions $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ can be described as fragments of the well known Keggin structure (Keggin, 1933). The Keggin structure $[\text{XW}_{12}\text{O}_{40}]^{z-}$ (where $X = \text{P}, \text{Si}, \text{Ge}, \text{C}$ or one of many other elements) is built up from twelve WO_6 octahedra. Three octahedra are connected by edges to four W_3O_{13} groups, which themselves form a polyanion with T_d symmetry by corner sharing. According to Baker & Figgis (1970), there are five possible isomers, α , β , γ , δ and ϵ , which differ by rotation of one, two, three or four W_3O_{13} groups by $\pi/3$. Until now, only the α and β isomers are known as isolated polyanions (Pope, 1983). Other isomers, such as ϵ , are known as polycations $\{[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$; Johansson, 1963} and as parts of larger structures (Khan, Müller, Dillinger,

Bögge, Chen & Zubieta, 1993). $\gamma\text{-}[\text{SiW}_{10}\text{O}_{36}]^{8-}$ can be described as a fragment of the γ -Keggin structure, removing those two octahedra which become edge-sharing by the rotation. The result is a lacunary structure with a central cavity above the SiO_4 tetrahedron. The symmetry of the polyanion is lowered from T_d to C_{2v} (Figs. 1 and 2).

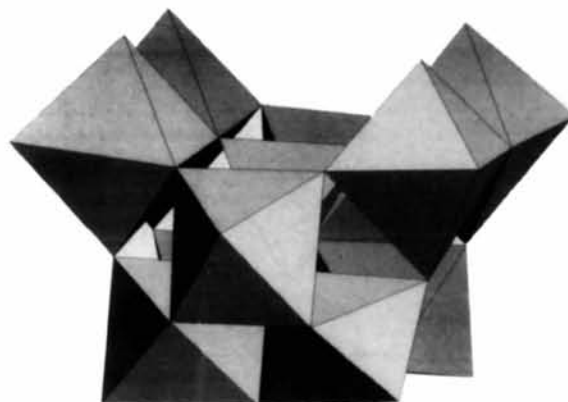


Fig. 1. Polyhedral representation of the polyanion, showing the central cavity (plane ac , 10° rotation of a).

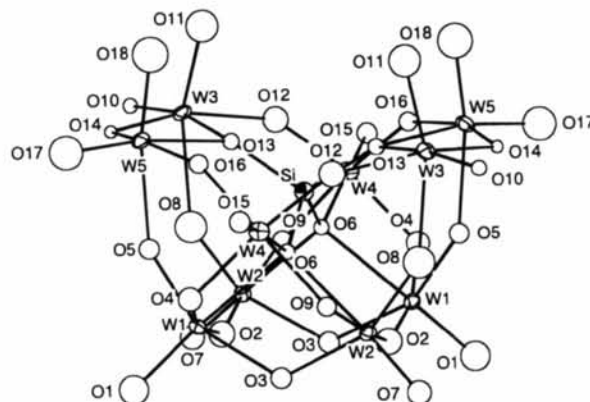


Fig. 2. Ball-and-stick representation of the polyanion (plane ac , 10° rotation of a).

The stability of the polyanion in solution depends on the size of the alkali metal cations, as reported by Canny, Tézé, Thouvenot & Hervé (1986). They investigated solutions of the lithium, sodium, potassium and rubidium salts and described the crystal structure of the rubidium salt. One Rb atom is located in the central cavity of the polyanion and seems to be responsible for its stability. Compounds of the $\gamma\text{-}[\text{SiW}_{10}\text{O}_{36}]^{8-}$ anion with cations smaller than potassium are not stable. The title structure completes the series of alkali metal salts of this type of lacunary polyanion.

There are five crystallographically independent Cs^+ cations with different coordination polyhedra in the

structure (see Table 2). Apart from Cs₂, all of these Cs⁺ cations are coordinated by water molecules as well as O atoms of the polyanions. The polyanions and Cs₂ form endless columns in the direction of the crystallographic *c* axis. Cs₂ is tenfold coordinated by four O atoms from the polyanion below and six from the polyanion above (Fig. 3). In contrast to the rubidium salt (Canny, Tézé, Thouvenot & Hervé, 1986), Cs₂ is not placed in the plane of the terminal O atoms, but a little above it. The reason may be the size of the cation as well as its coordination to the polyanion above.

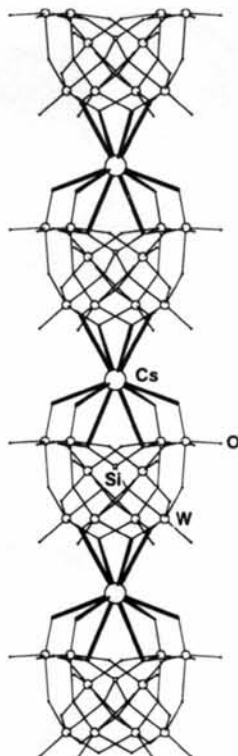


Fig. 3. A SCHAKAL88 (Keller, 1988) plot of the coordination sphere of Cs₂. For clarity, the polyanions are represented by lines (plane *bc*, 45° rotation of *c*).

There are four short (3.19 Å), four medium (3.26 Å) and two long Cs—O distances (3.46 Å). The two long distances are between Cs₂ and two O atoms from the SiO₄ tetrahedron. The short bonds are between Cs and the terminal O atoms. In Fig. 4, a view of the central cavity is presented, showing the fit of the cation between the terminal O atoms.

The importance of the nature of the counterion for the stability of the polyanion is obvious. On the one hand, one can compare the polyanions and their oxygen surfaces with metal oxide structures, while on the other hand, the cavity of terminal O atoms in lacunary structures can be compared with organic structures

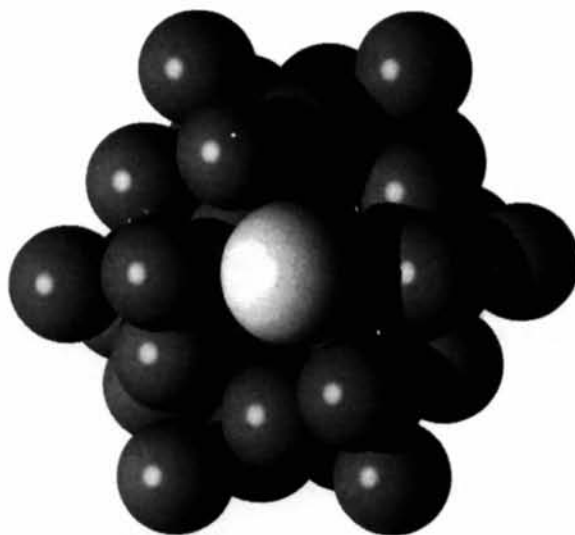


Fig. 4. Space-filling representation of the polyanion [$r(\text{Cs}^+) = 1.7 \text{ \AA}$, $r(\text{O}^{2-}) = 1.35 \text{ \AA}$, SCHAKAL88 (Keller, 1988) plot, plane *ab*].

such as crown ethers, the stability of the alkali metal complexes of which depends on the size of the alkali metal cations (Pedersen & Frensdorff, 1972).

Experimental

The title compound was obtained by filtering a solution of Cs₂WO₄ (pH 8) through a glass frit, forming large clear single crystals (the glass frit being the source of the silica). A crystalline powder of the same compound can be obtained by precipitation of a solution of γ -K₈[SiW₁₀O₃₆].*x*H₂O with CsCl. The potassium salt was obtained as described by Canny, Tézé, Thouvenot & Hervé (1986). The caesium salt was characterized by IR and Raman spectra.

Crystal data

Cs₈[SiW₁₀O₃₆].9H₂O
M_r = 3667.9
 Orthorhombic
*P*2₁2₁2
a = 12.552 (3) Å
b = 19.180 (3) Å
c = 9.997 (2) Å
V = 2406.8 (8) Å³
Z = 2
D_x = 4.999 Mg m⁻³

Mo *K*α radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 20 reflections
 $\theta = 10\text{--}18^\circ$
 $\mu = 31.389 \text{ mm}^{-1}$
T = 293 K
 Spherical
 0.45 × 0.45 × 0.45 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical (Xtal3.2; Hall, Flack & Stewart, 1992)
T_{min} = 0.0158, *T_{max}* = 0.0342
 7190 measured reflections
 3082 independent reflections

2952 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.048
 $\theta_{\text{max}} = 27.43^\circ$
h = -12 → 16
k = -18 → 24
l = -12 → 12
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.5%

Refinement

Refinement on F $R = 0.07$ $wR = 0.07$ $S = 4.232$

2952 reflections

175 parameters

H atoms not located

Weighting scheme based

on measured e.s.d.'s

 $(\Delta/\sigma)_{\max} = 0.45$ $\Delta\rho_{\max} = 5.95 \text{ e } \text{\AA}^{-3}$ (near Cs and W) $\Delta\rho_{\min} = -3.98 \text{ e } \text{\AA}^{-3}$ (near Cs and W)

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV, Tables

2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) U_{iso} for Si and O; $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$ for W and Cs.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
W1	0.5779 (1)	0.37995 (8)	0.9281 (2)	0.0238
W2	0.3097 (1)	0.45765 (9)	0.9291 (2)	0.0237
W3	0.7894 (1)	0.10114 (9)	0.7093 (2)	0.0258
W4	0.7596 (1)	0.42341 (9)	1.1533 (2)	0.0263
W5	0.5264 (1)	0.32906 (9)	1.2901 (2)	0.0267
Cs1	0.3547 (4)	0.1370 (3)	1.2716 (5)	0.093
Cs2	1/2	1/2	0.5789 (5)	0.055
Cs3	0.3485 (3)	0.2843 (2)	0.6666 (3)	0.052
Cs4	1	1/2	1.3737 (6)	0.060
Cs5	0.5750 (2)	0.1775 (2)	0.9907 (3)	0.042
Si	1/2	1/2	1.173 (2)	0.025 (4)
O1	0.596 (2)	0.311 (2)	0.810 (4)	0.049 (9)
O2	0.442 (2)	0.420 (2)	0.881 (3)	0.038 (8)
O3	0.649 (2)	0.458 (1)	0.838 (3)	0.029 (6)
O4	0.717 (2)	0.358 (1)	1.013 (3)	0.034 (8)
O5	0.527 (2)	0.337 (1)	1.072 (3)	0.030 (7)
O6	0.605 (2)	0.470 (1)	1.076 (3)	0.025 (6)
O7	0.230 (2)	0.415 (1)	0.828 (3)	0.037 (8)
O8	0.810 (3)	0.095 (2)	0.934 (4)	0.06 (1)
O9	0.198 (2)	0.513 (1)	1.009 (3)	0.027 (6)
O10	0.666 (2)	0.140 (1)	0.718 (3)	0.025 (6)
O11	0.308 (3)	0.417 (2)	0.465 (3)	0.06 (1)
O12	0.754 (2)	0.500 (2)	1.262 (3)	0.038 (7)
O13	0.453 (2)	0.430 (1)	0.266 (3)	0.025 (7)
O14	0.375 (2)	0.315 (1)	1.276 (3)	0.020 (6)
O15	0.382 (2)	0.111 (1)	0.800 (3)	0.029 (7)
O16	0.660 (2)	0.372 (1)	1.268 (3)	0.025 (6)
O17	0.561 (3)	0.248 (2)	1.279 (4)	0.06 (1)
O18	0.520 (3)	0.341 (2)	0.456 (4)	0.06 (1)
O1W	0.267 (2)	0.057 (1)	1.443 (3)	0.037 (7)
O2W	0.365 (4)	0.245 (3)	0.986 (5)	0.09 (1)
O3W	0.214 (4)	0.225 (2)	0.428 (4)	0.09 (1)
O4W	0.485 (3)	0.171 (2)	0.519 (4)	0.07 (1)
O5W	1/2	0	1.094 (6)	0.07 (2)

Table 2. Selected geometric parameters (\AA)

W1—O1	1.78 (3)	Cs1 ^{III} —O3W ^{III}	2.90 (4)
W1—O2	1.93 (3)	Cs1 ^{III} —O4W ^{III}	3.04 (4)
W1—O3	1.96 (3)	Cs2—O2	3.47 (3)
W1—O4	1.98 (3)	Cs2—O3	3.29 (3)
W1—O5	1.78 (3)	Cs2—O11	3.11 (4)
W1—O6	2.30 (3)	Cs2—O13	3.45 (3)
W2—O2	1.87 (3)	Cs2—O18	3.31 (4)
W2—O9	1.94 (3)	Cs2—O2 ^{II}	3.47 (3)
W2—O7	1.64 (3)	Cs2—O3 ^{II}	3.29 (3)
W2—O8 ^I	1.70 (4)	Cs2—O11 ^{II}	3.11 (4)
W2—O3 ^{II}	1.93 (3)	Cs2—O13 ^{II}	3.45 (3)
W2—O6 ^{II}	2.29 (3)	Cs2—O18 ^{II}	3.31 (4)
W3—O8	2.27 (4)	Cs3—O1	3.46 (3)
W3—O10	1.73 (2)	Cs3—O11	3.28 (3)
W3 ^{III} —O11 ^{III}	1.79 (3)	Cs3—O18	3.20 (4)
W3 ^{III} —O13 ^{III}	2.16 (3)	Cs3—O7	3.33 (3)
W3 ^{III} —O12 ^{III}	2.04 (3)	Cs3—O3W	3.13 (4)
W3 ^{III} —O14 ^{III}	1.95 (2)	Cs3—O4W	3.13 (4)
W4—O4	1.96 (3)	Cs3—O2W	3.29 (5)
W4—O6	2.27 (2)	Cs4—O12	3.28 (3)

W4—O12	1.83 (3)	Cs4—O15 ^{III}	3.12 (3)
W4—O15 ^{III}	1.73 (3)	Cs4—O4W ^{III}	3.46 (4)
W4—O16	1.96 (3)	Cs4—O12 ^I	3.28 (3)
W4—O9 ^{II}	1.96 (3)	Cs4—O15 ^{II}	3.12 (3)
W5—O5	2.18 (3)	Cs4—O4W ^{II}	3.46 (4)
W5—O16	1.88 (3)	Cs5 ^{III} —O7 ^{III}	3.19 (3)
W5—O13 ^{III}	2.15 (3)	Cs5—O8	3.39 (4)
W5—O18 ^{III}	1.67 (4)	Cs5—O10	3.04 (3)
W5—O14	1.93 (2)	Cs5—O15	3.34 (3)
W5—O17	1.62 (3)	Cs5—O17	3.18 (4)
Cs1 ^I —Cs5	4.017 (6)	Cs5—O2W	2.93 (5)
Cs1 ^{III} —O1	3.49 (3)	Cs5—O1	3.15 (3)
Cs1 ^{III} —O3	3.35 (3)	Cs5—O5	3.22 (3)
Cs1 ^{III} —O4	3.33 (3)	Si—O6	1.73 (3)
Cs1—O14	3.42 (2)	Si—O13 ^{III}	1.74 (3)
Cs1—O17	3.35 (3)	Si—O6 ^I	1.73 (3)
Cs1—O1W	2.55 (3)	Si—O13 ^I	1.74 (3)

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

W and Cs atoms were refined anisotropically, Si and O atoms were refined isotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.2 AD-DREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); *Xtal3.2*. Program(s) used to refine structure: *Xtal3.2 CRYLSQ*. Molecular graphics: *ORTEPII* (Johnson, 1977); *SCHAKAL88* (Keller, 1988); *ATOMS* (Dowty, 1991). Software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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