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$Na_{8.5}H_{1.5}[GeW_9O_{34}]\cdot 20H_2O$ containing trivacant A-α- and A-β-Keggin anions

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(Ge–O) = 0.013 Å
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.076
wR factor = 0.163
Data-to-parameter ratio = 24.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, 8.5-sodium 1.5-hydrogen tetratriacontaoxononatungstomonogermanate(10−) icosahydrate, contains A-α- and A-β-type trivacant Keggin $[GeW_9O_{34}]^{10-}$ anions, which are disordered in an approximately 1:9 ratio. Pairs of anions related by a center of symmetry are linked *via* O—Na—O bonding to form a quasi-sandwich-type $[Na_{10}(H_2O)_{14}(GeW_9O_{34})_2]^{10-}$ complex.

Comment

The $[XW_9O_{34}]^{10-}$ (X = Si, Ge) species (Hervé & Tézé, 1977) is one of the popular trivacant Keggin anions, which is derived from the parent Keggin $[XW_{12}O_{40}]^{4-}$ anion by eliminating three WO_6 octahedra (a W_3O_6 unit). Four structural isomers are possible for $[XW_9O_{34}]^{10-}$: A-α, A-β, B-α, and B-β. The A-α and A-β isomers are formed by removal of three corner-shared WO_6 octahedra from α- and β-$[XW_{12}O_{40}]^{4-}$, respectively; likewise the B-α and B-β isomers by removal of three edge-shared WO_6 octahedra. The resulting 'incomplete'

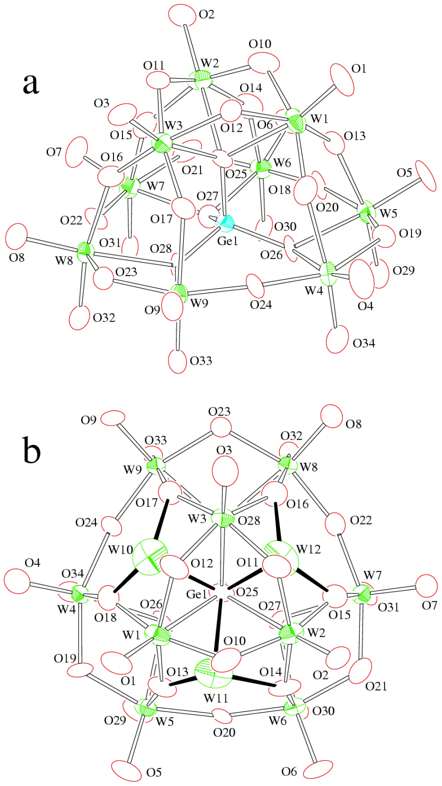

Figure 1
*ORTEP*II (Johnson, 1976) drawings of the $[GeW_9O_{34}]^{10-}$ anion, showing (*a*) the A-β-isomer only and (*b*) the A-β-isomer with atoms W10, W11 and W12 of the α-isomer, viewed along the C_3 axis. The filled bonds link W10–W12 and O ligands of the anion. The filled displacement ellipsoids are drawn at the 50% probability level.

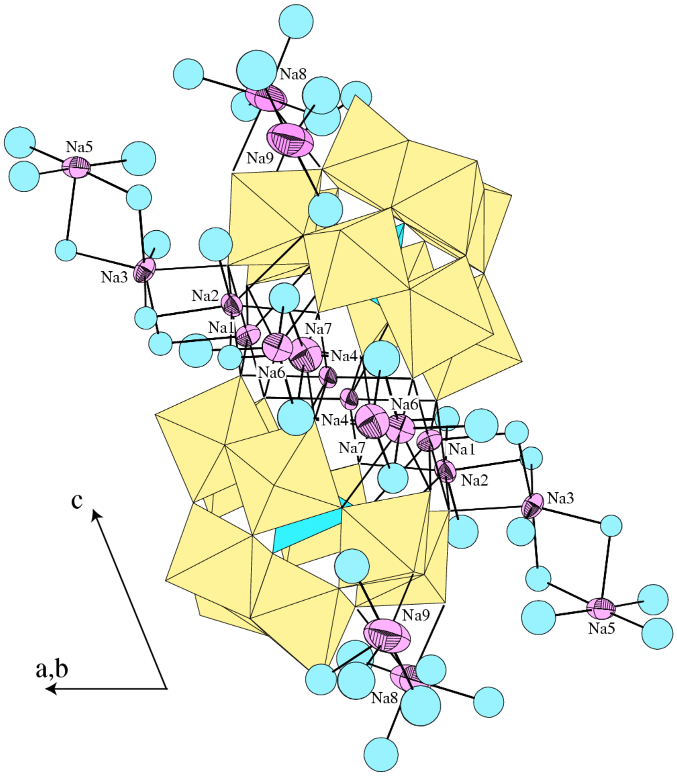

Figure 2
View of the $[Na_{10}(H_2O)_{14}(GeW_9O_{34})_2]^{10-}$ complex and other NaO_n groups. Shaded pink ellipsoids and blue spheres denote Na and aqua ligands, respectively. The displacement ellipsoids are drawn at the 50% probability level. Only Na atoms are labeled.

anions tend to bind external metal cations and organometalloidal groups which refill the vacancies to yield mixed-metal 'complete' Keggin structures. Such examples are mainly of the A-α and A-β types, *viz*. A-β-$[SiW_9Al_3O_{37}(H_2O)_6]^{7-}$ (Chen, Qu, Peng, Lin & Yu, 1993), A-α-$[SiCr_3W_9O_{37}(H_2O)_3]^{7-}$ (Wassermann *et al.*, 1994), $[\{A\text{-}\alpha\text{-}SiW_9O_{30}Cr_3(OH)_3\}_2(OH)_3]^{11-}$ (Wassermann *et al.*, 1995), A-α-$[GeW_9V_3O_{40}]^{4-}$ (Chen, Qu, Peng, Yu, Lin & Yu, 1993), $[\{A\text{-}\alpha\text{–}GeW_9Ti_3O_{37}\}_2O_3]^{14-}$ (Yamase *et al.*, 1993), *etc*. Recently, interest has also been focused on intense second harmonic generation (SHG) by polycrystalline salts of $[XW_9O_{34}]^{10-}$ (X = Si, Ge) (Murakami *et al.*, 2001). Although structures of A-α- and A-β-$[SiW_9O_{34}]^{10-}$ have been reported (Hubert & Hartl, 1996; Robert & Tézé, 1981), those of Ge analogs are still undetermined. Here we report the first structural characterization of $[GeW_9O_{34}]^{10-}$.

The crystal structure of $Na_{8.5}H_{1.5}[GeW_9O_{34}]\cdot 20H_2O$ is isomorphous with $Na_9H[SiW_9O_{34}]\cdot 23H_2O$ (Robert & Tézé, 1981) and $Na_7H_2[PW_9O_{34}]\cdot 20H_2O$ (He *et al.*, 2002). Fig. 1(*a*) shows the A-β-$[GeW_9O_{34}]^{10-}$ anion, which possesses an approximate C_{3v} symmetry, consisting of one edge-sharing W_3O_{13} group of [W1W2W3] sitting in the 'cap' position (W_{cap}), three edge-sharing W_2O_{10} groups of [W4W5], [W6W7] and [W8W9] in 'belt' positions (W_{belt}), and a central GeO_4. There are several types of O atoms in the anion, *viz*. O*a* (O25–O28) atoms are bonded to Ge and two or three W atoms, corner-sharing O*b* (O13, O14, O15, O16, O17 and O18) and O*b*′ (O20, O22 and O24) atoms, edge-sharing O*c* (O10, O11 and O12) and O*c*′ (O19, O21 and O23) atoms, and the terminal O*d* (O1–O9) and O*d*′ (O29, O30, O31, O32, O33 and O34) atoms. The interatomic distances are summarized in Table 1. The GeO_4 tetrahedron is nearly regular, as observed in $[(A\text{-}\alpha\text{-}GeW_9Ti_3O_{37})_2O_3]^{14-}$ (Yamase *et al.*, 1993). The W atoms in $W_{belt}O_6$ octahedra are significantly off-centered toward the O*d*—O*d*′ edges; thereby distances of W_{belt}—O*b* (mean 2.142 Å) are much longer than those of W_{belt}—O*b*′ (mean 1.903 Å) and W_{cap}—O*b* (mean 1.878 Å). The W_{belt}—O*a* (mean 2.24 Å) are somewhat shorter than W_{cap}—O*a* (mean 2.30 Å). All geometrical features of the A-β-$[GeW_9O_{34}]^{10-}$ anion are similar to those of A-β-$[SiW_9O_{34}]^{10-}$ (Robert & Tézé, 1981) and A-β-$[PW_9O_{34}]^{9-}$ (He *et al.*, 2002). It is worth noting that additional W10, W11 and W12 atoms have been found in the vicinity of O12, O10 and O11 atoms, respectively (Fig. 1*b*). These W atoms are of the A-α-isomer, which is formed by 60° rotation of the capping W_3O_{13} group about the C_3 axis of the anion. Refinement of occupancy revealed that the A-α- and B-β-isomers co-exist in an approximate 1:9 ratio (see details of the refinement). The bridging atoms O13, O14, O15, O16, O17, O18 and O25 are common to both isomers. Three terminal and three bridging O atoms which should be attached to W10, W11 and W12 could not be located by X-ray diffraction analysis because of the low electron density (8/10 electrons per atom).

Bonding among $[GeW_9O_{34}]^{10-}$, Na^+, and aqua-ligands is shown in Fig. 2. Each Na atom is penta-, hexa- or hepta-coordinated by aqua ligands and/or the O atoms of the anion (Na—O <3.1 Å). All of the resulting NaO_n polyhedra except for $Na8O_6$ and $Na9O_5$ share their edges to form a belt-shape $\{Na_{14}O_{18}(H_2O)_{28}\}_\infty$ chain running along the $[1\bar{1}0]$ direction (Fig. 3). Two symmetry-related $[GeW_9O_{34}]^{10-}$ anions are coupled by atoms Na1, Na2, Na4, Na6, and Na7 through O*a* (O26, O27 and O28) and O*d*′ atoms, giving rise to a quasi-sandwich-type centrosymmetric $[Na_{10}(H_2O)_{14}(GeW_9O_{34})_2]^{10-}$ complex (Fig. 2). This type of dimerization has been observed in isomorphous $Na_9H[SiW_9O_{34}]\cdot 23H_2O$ (Robert & Tézé, 1981) and $Na_7H_2[PW_9O_{34}]\cdot 20H_2O$ (He *et al.*, 2002), although the Na4 position in Fig. 3 is vacant in the latter compound. $Na8O_6$ interlinks the $\{Na_{14}O_{18}(H_2O)_{28}\}_\infty$ chains, while $Na9O_5$ is isolated from other NaO_n polyhedra.

Experimental

An aqueous (150 ml) solution of $Na_2WO_4\cdot 2H_2O$ (90 g) was added to an aqueous (50 ml) solution of GeO_2 (4.7 g) and NaOH (5 g). Concentrated hydrochloric acid (*ca* 40 ml) was poured slowly into the vigorously stirred solution until pH = 7. The white supernatant solution was heated under reflux for 1 h. After it cooled to room temperature, the impurities formed were removed by filtration and solid Na_2CO_3 (20 g) was added to the filtrate. The resulting white precipitate was collected by filtration, washed with cold water and methanol, and dried in vacuum to yield a powder of the crude product (yield 34.1 g, 35% based on W). It was recrystallized from hot water to give colorless single crystals. Found: H 1.2, O 29.0, Na 7.0, Ge 3.2, W 59.6%; calculated for $Na_{8.5}H_{1.5}[GeW_9O_{34}]\cdot 20H_2O$: H 1.46, O 30.54, Na 6.91, Ge 2.57, W 58.52%.

Crystal data

$Na_{8.5}H_{1.5}[GeW_9O_4]\cdot 20H_2O$
$M_r = 2828.45$
Triclinic, $P\overline{1}$
$a = 12.6563$ (9) Å
$b = 13.260$ (1) Å
$c = 18.491$ (2) Å
$\alpha = 72.576$ (3)°
$\beta = 70.078$ (3)°
$\gamma = 62.848$ (3)°
$V = 2557.3$ (3) $Å^3$

$Z = 2$
$D_x = 3.673$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11591 reflections
$\theta = 2.3$–$30.0°$
$\mu = 20.95$ mm^{-1}
$T = 296.2$ K
Block, colorless
0.15 × 0.15 × 0.08 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: numerical (Higashi, 1995)
$T_{min} = 0.041$, $T_{max} = 0.173$
18 682 measured reflections

14 391 independent reflections
9852 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.075$
$\theta_{max} = 30.0°$
$h = -17 \rightarrow 17$
$k = -18 \rightarrow 16$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.163$
$S = 1.56$
14 383 reflections
586 parameters

H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 4.29$ e $Å^{-3}$
$\Delta\rho_{min} = -3.55$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å).

W1—O1	1.77 (1)	W5—O26	2.25 (1)
W1—O13	1.82 (1)	W6—O6	1.75 (1)
W1—O18	1.92 (1)	W6—O30	1.76 (1)
W1—O12	1.98 (1)	W6—O20	1.87 (1)
W1—O10	1.98 (1)	W6—O21	1.92 (1)
W1—O25	2.29 (1)	W6—O14	2.15 (1)
W2—O2	1.75 (1)	W6—O27	2.26 (1)
W2—O14	1.89 (1)	W7—O7	1.73 (1)
W2—O15	1.94 (1)	W7—O31	1.78 (1)
W2—O11	1.96 (1)	W7—O22	1.90 (1)
W2—O10	1.96 (2)	W7—O21	1.95 (1)
W2—O25	2.34 (1)	W7—O15	2.10 (1)
W3—O3	1.77 (1)	W7—O27	2.25 (1)
W3—O17	1.84 (1)	W8—O32	1.76 (1)
W3—O16	1.86 (1)	W8—O8	1.77 (1)
W3—O12	1.94 (1)	W8—O22	1.92 (1)
W3—O11	1.98 (1)	W8—O23	1.98 (1)
W3—O25	2.28 (1)	W8—O16	2.12 (1)
W4—O4	1.73 (1)	W8—O28	2.26 (1)
W4—O34	1.77 (1)	W9—O9	1.75 (1)
W4—O24	1.90 (1)	W9—O33	1.76 (1)
W4—O19	1.94 (1)	W9—O24	1.90 (1)
W4—O18	2.19 (1)	W9—O23	1.94 (1)
W4—O26	2.24 (1)	W9—O17	2.16 (1)
W5—O29	1.73 (1)	W9—O28	2.218 (10)
W5—O5	1.75 (1)	Ge1—O26	1.75 (1)
W5—O20	1.94 (1)	Ge1—O27	1.759 (9)
W5—O19	1.94 (1)	Ge1—O28	1.77 (1)
W5—O13	2.14 (1)	Ge1—O25	1.78 (1)

Of all the independent reflections, eight were omitted because of observation errors. All of the atoms except for the water of crystallization were refined anisotropically. Na4 was refined with half-occupancy because the displacement parameter was too large in the refinement under full-occupancy. During the refinement, three large Fourier peaks occurred near atoms O10, O11 and O12. The peaks were assigned as W10, W11 and W12 of the A-α-isomer, which are disordered with atoms W1, W2 and W3 of the A-β-isomer (see *Comment*). Therefore, the site occupancies of W10/W11/W12 and W1/W2/W3 were set as common parameters ($O_{cc\alpha}$ and $O_{cc\beta}$, respectively) and refined under the condition of $O_{cc\alpha} + O_{cc\beta} = 1.0$, resulting in $O_{cc\alpha}:O_{cc\beta} = 0.103:0.897(2) \simeq 0.1:0.9$. Therefore, site occupancies of O1, O2, O3, O10, O11 and O12, associated with the A-β-isomer, were fixed at 0.9. Six (three bridging and three terminal) O atoms related to the A-α-isomer could not be found in difference Fourier maps because of their low electron densities (see *Comment*). Residual difference Fourier peaks with $\Delta\rho_{max} = 4.29$ e $Å^{-3}$ and $\Delta\rho_{min} = -3.55$ e $Å^{-3}$ are observed at positions 0.974 and 0.681 Å from W4 and W9, respectively.

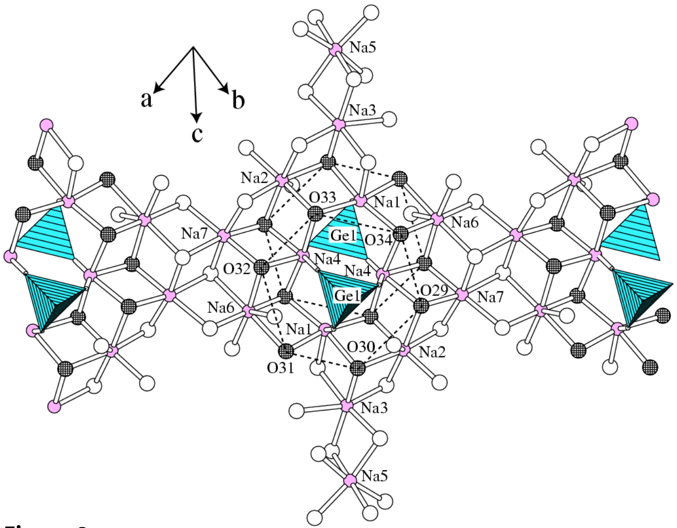

Figure 3
View of the $[Na_{14}O_{18}(H_2O)_{28}]_\infty$ chain and GeO_4 tetrahedra. Pink and white spheres denote Na and O atoms, respectively. Cross-hatched spheres represent O*d*′ atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *teXsan* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SYSTEM*90 (Hou *et al.*, 1994); program(s) used to refine structure: *teXsan*; molecular grahics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *teXsan*.

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