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The crystal structure of $\text{KNa}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$ exhibiting a $\infty[\text{Te}_4\text{O}_9]^{2-}$ layer

Table 1: Data collection and handling.

Crystal:	Colorless plate-like
Size:	0.16 × 0.15 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	9.06 mm ⁻¹
θ_{max} , completeness:	27.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11,149, 3028, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2970
$N(\text{param})_{\text{refined}}$:	204
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

thoroughly mixed and sealed in a stainless autoclave with a 23 mL Teflon liner. The mixture was heated at 463 K in an oven for three days, and then cooled to room temperature at a rate of 6 K/h. Colorless plate-like crystals of $\text{KNa}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$ were collected and washed with purified water.

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Abstract

$\text{KNa}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.5701(4)$ Å, $b = 8.7278(4)$ Å, $c = 10.4082(5)$ Å, $\alpha = 67.582(2)^\circ$, $\beta = 66.167(2)^\circ$, $\gamma = 77.861(2)^\circ$, $V = 656.85(6)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0180$, $wR_{\text{ref}}(F^2) = 0.0452$, $T = 296(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All starting materials were from commercial sources and used without further purification. The reagents of 2 mmol NaOH, 4 mmol TeO_2 , 1 mmol KF, and 2 mL H_2O were

Experimental details

The structure was solved by direct method with SHELXS and further refined with the SHELXL program. The oxygen-bound H atoms were located on a difference Fourier map and refined with distances O–H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Comment

Metal tellurites with lone-pair electrons have received great attention owing to their structural diversity and potential applications such as in the field of piezoelectricity, pyroelectricity, and second-order nonlinear optics [4–7]. Usually, the Te(IV)–O units can adopt three geometry patterns in various crystal structures: TeO_3 trigonal pyramid, TeO_4 sphenoid, and TeO_5 distorted square pyramid. The three types of Te–O units can further build up a large number of structural motifs when connected with each other or with other atomic groups. Such examples include the recently synthesized hexamolybdotellurates $\text{A}_4\text{Mo}_6\text{TeO}_{22}\cdot 2\text{H}_2\text{O}$ ($\text{A} = \text{NH}_4, \text{Rb}$) and $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot$

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.5000	0.5000	0.5000	0.0718 (7)
Na1	0.5000	0.0000	0.0000	0.0719 (12)
Na2	0.6282 (2)	0.60310 (19)	0.04273 (17)	0.0271 (3)
Te1	0.14045 (3)	0.15162 (2)	0.66373 (2)	0.01183 (6)
Te2	0.17769 (3)	0.52011 (3)	0.30803 (2)	0.01277 (6)
Te3	0.17926 (3)	−0.17465 (3)	0.97812 (2)	0.01326 (6)
Te4	0.46186 (3)	0.17301 (3)	0.32481 (2)	0.01295 (6)
O1	0.6810 (3)	0.1596 (3)	0.3230 (3)	0.0196 (5)
O2	0.3696 (3)	0.2070 (3)	0.5341 (3)	0.0189 (5)
O3	0.4302 (3)	0.4056 (3)	0.2427 (3)	0.0255 (6)
O4	0.1931 (3)	0.0903 (3)	0.8377 (3)	0.0164 (5)
O5	−0.1541 (3)	0.1123 (3)	0.8632 (3)	0.0194 (5)
O6	0.0960 (3)	0.3129 (3)	0.3831 (3)	0.0195 (5)
O7	0.5801 (3)	0.1798 (3)	0.0978 (3)	0.0196 (5)
O8	0.0787 (3)	0.3772 (3)	0.6528 (3)	0.0186 (5)
O9	0.2022 (4)	0.5754 (3)	0.1066 (3)	0.0247 (6)
O10	0.7538 (5)	0.2273 (5)	0.5285 (4)	0.0471 (9)
H1	0.715 (6)	0.199 (8)	0.478 (6)	0.071*
H2	0.859 (3)	0.246 (8)	0.480 (6)	0.071*
O11	0.5128 (4)	0.7766 (4)	0.2051 (3)	0.0278 (6)
H3	0.600 (3)	0.803 (6)	0.209 (5)	0.042*
H4	0.423 (3)	0.799 (6)	0.271 (4)	0.042*
O12	0.2025 (5)	0.1862 (4)	0.1443 (4)	0.0415 (8)
H5	0.163 (7)	0.101 (5)	0.151 (6)	0.062*
H6	0.149 (7)	0.211 (7)	0.224 (4)	0.062*
O13	0.8193 (6)	0.4849 (5)	0.1685 (6)	0.0664 (14)
H7	0.922 (4)	0.505 (9)	0.113 (7)	0.100*
H8 ^a	0.786 (11)	0.534 (16)	0.233 (11)	0.100*
H9 ^b	0.810 (11)	0.381 (2)	0.210 (16)	0.100*

^aOccupancy: 0.53(3), ^bOccupancy: 0.47(3).

$2\text{H}_2\text{O}$, which are built by the $[\text{Mo}_6\text{O}_{22}]^{8-}$ group with TeO_4 units as connectors [8, 9]. Further rich examples are the alkali-metal tellurites, including Na_2TeO_3 [10], $\text{Na}_2\text{Te}_2\text{O}_5\cdot 2\text{H}_2\text{O}$ [11], $\text{Na}_4\text{Te}_4\text{O}_{10}$ [12], $\text{K}_2\text{Te}_4\text{O}_9\cdot 3.2\text{H}_2\text{O}$ [13], $\text{K}_2\text{Te}_4\text{O}_9$ [14]. Chen *et al.* discussed that the size of alkali-metal cations, H_2O molecules, and the interaction between framework oxygen atoms and alkali cations can play great roles in the formation of centric-acentric structure for the alkali-metal tellurites [15]. Here we synthesized the title new double alkali-metal tellurite to provide further insight on the intrinsic mechanism of centric-acentric formation of alkali-metal tellurites.

The title compound contains the $[\text{Te}_4\text{O}_9]^{2-}$ anion layered structure that has been found in the double alkali-metal tellurite $\text{RbK}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$. However, different to the noncentrosymmetric structure of $\text{RbK}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$, substitution of Rb and K with the corresponding smaller K and Na leads to a centrosymmetric structure of $\text{KNa}_3\text{Te}_8\text{O}_{18}\cdot 5\text{H}_2\text{O}$

[15]. There are two kinds of Te–O connection fashions, i.e., $\text{Te}(1)\text{O}_3$ in trigonal pyramid, and $\text{Te}(2)$ – $\text{Te}(4)$ are in TeO_4 sphe- noid structures. $\text{Te}(2)\text{O}_4$, $\text{Te}(3)\text{O}_4$, and $\text{Te}(4)\text{O}_4$ sphe- noids are connected to each other through corner-sharing to form a $[\text{Te}_6\text{O}_{12}\text{O}_{12/2}]$ pentagonal ring. The $\text{Te}(1)\text{O}_3$ trigonal pyramid connects three neighboring $[\text{Te}_6\text{O}_{12}\text{O}_{12/2}]$ pentag- onal ring up to the $[\text{Te}_4\text{O}_9]^{2-}$ anion layer. The bond valence sums (BVS) are calculated to be 3.66, 4.02, 3.95, and 4.02 for central cations $\text{Te}(1)$, $\text{Te}(2)$, $\text{Te}(3)$, and $\text{Te}(4)$, respec- tively [16]. K^+ and Na^+ cations lie between the layers for charge balance, and the water molecules are arranged around the K^+ cations to separate them with Na^+ cations. The K–O distances are distributed in the range of 2.847– 3.074 $\text{\AA}$ when the nearest six oxygen atoms are considered, and the BVS of the K^+ cation is calculated to be 0.71, indi- cating that some more oxygen neighbors still contribute. $\text{Na}(1)$ cation is coordinated by eight oxygen atoms with Na–O distances of 2.301–2.919 $\text{\AA}$ with BVS = 1.03, and $\text{Na}(2)$ is coordinated by six oxygen atoms with Na–O distances of 2.321–2.737 $\text{\AA}$ with BVS = 1.09.

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