

Hansesmarkite, $\text{Ca}_2\text{Mn}_2\text{Nb}_6\text{O}_{19}\cdot 20\text{H}_2\text{O}$, a new hexaniobate from a syenite pegmatite in the Larvik Plutonic Complex, southern Norway

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ABSTRACT

The new mineral hansesmarkite (IMA2015-067), $\text{Ca}_2\text{Mn}_2\text{Nb}_6\text{O}_{19}\cdot 20\text{H}_2\text{O}$, was discovered at the AS Granit larvikite quarry in Tvedalen, Larvik, Vestfold, Norway. Hansesmarkite forms faintly yellow crystals up to 0.3 mm or thin coatings in patches on gonnardite. Hansesmarkite is biaxial (+) with refractive indices (white light): $\alpha = 1.683(2)$, $\beta = 1.698(2)$ and $\gamma = 1.745(3)$; $2V_{(\text{meas.})} = 60.7(6)^\circ$ and $2V_{(\text{calc.})} = 60.3^\circ$. The mineral exhibits moderate dispersion ($r > v$) and is pleochroic with X (almost colourless) $< Y$ (pale yellow) $\ll Z$ (orangey yellow). The optical orientation is $X \wedge c = 20^\circ$, $Y \wedge b = 16^\circ$ and $Z \wedge a = 5^\circ$. The empirical formula based on five electron probe microanalyses and calculated based on Nb = 6 apfu is $(\text{Ca}_{1.93}\text{Na}_{0.02}\text{K}_{0.01})_{\Sigma 1.96}(\text{Mn}_{1.79}\text{Fe}_{0.11})_{\Sigma 1.90}\text{Nb}_6\text{O}_{18.84}\cdot 20\text{H}_2\text{O}$, with H_2O determined from the structure solution. The mineral is triclinic, $P\bar{1}$, with $a = 9.081(4)$, $b = 9.982(8)$, $c = 10.60(1)$ Å, $\alpha = 111.07(8)$, $\beta = 101.15(6)$, $\gamma = 99.39(5)^\circ$, $V = 850.8(13)$ Å³ and $Z = 1$. The structure was solved at 120 K because of thermal instability of the mineral and refined to $R_1 = 2.50\%$ for $F_o > 4\sigma$. The strongest reflections in the x-ray diffraction diagram are: [$d_{\text{obs.}}$ in Å (I)(hkl)] 9.282(36)(001), 8.610(100)(100, 01 $\bar{1}$), 3.257(30)(03 $\bar{1}$, 1 $\bar{3}$ 1) and 3.058(18)(1 $\bar{3}$ 0, 2 $\bar{1}$ 2). Hansesmarkite is the third naturally occurring hexaniobate in which six edge-sharing Nb-octahedra form the Lindqvist ion. These are linked via Mn-octahedra forming rods along [100] and Ca is located between the rods, creating a three dimensional structure via hydrogen bonds.

KEYWORDS: hexaniobate, Lindqvist ion, hansesmarkite, new mineral, Larvik Plutonic Complex, syenite pegmatite.

Introduction

HANSESMARKITE is the third naturally occurring hexaniobate to be described; peterandresenite, $\text{Mn}_4\text{Nb}_6\text{O}_{19}\cdot 14\text{H}_2\text{O}$, was the first (Friis *et al.*, 2014) and melcherite, $(\text{Ba,K})_2(\text{Na,Ca})_2\text{MgNb}_6\text{O}_{19}\cdot 6\text{H}_2\text{O}$, the second (Andrade *et al.*, 2015). The mineral had been identified initially as peterandresenite, but the difference in colour led one of the authors (HF) to re-examine the material. Hexaniobates are a class of compounds

collectively called polyoxoniobates (PONb) that are characterized by large ions formed by multiple NbO_6 octahedra. Although hexaniobates are rare in nature, they have attracted much attention in recent years in inorganic chemistry (for a review see Nyman, 2011). In hexaniobates, the PONb ion consists of six edge-sharing NbO_6 octahedra, arranged in a large ‘super octahedron’ referred to as the Lindqvist ion (Lindqvist, 1953). In addition to the three naturally occurring hexaniobates, two other PONb minerals have been described, namely menezesite and aspedamite (Atencio *et al.*, 2008; Cooper *et al.*, 2012). In contrast to the hexaniobates, these structures contain a heteropolyoniobate ion.

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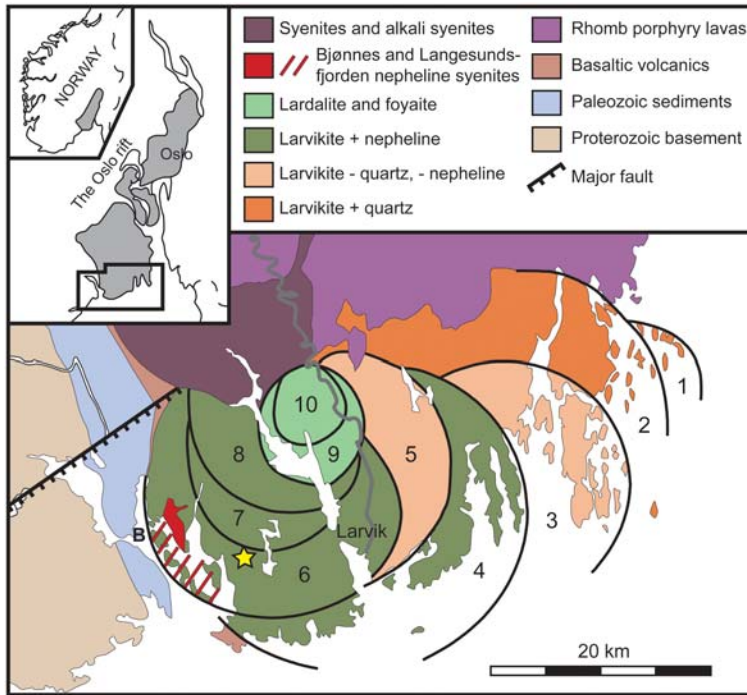


FIG. 1. Simplified geological map of the Larvik Plutonic Complex (LPC) with the various ring sections shown as well as the town of Brevik (B) and the AS Granit quarry (star). Modified after Petersen (1978) and Dahlgren (2010).

The mineral is named in honour of Hans Morten Thrane Esmark (1801–1882), a Norwegian priest from the town of Brevik situated by the Langesundsfjord west of the Larvik Plutonic Complex (LPC) (Fig. 1) and the son of Jens Esmark, head of the mining academy in Kongsberg and later the first professor in geology at the University of Oslo. Hans M. T. Esmark was an enthusiastic mineral collector in the pegmatites of the LPC and discovered several new mineral species. Some were later discredited, but aegirine, leucophanite and thorite are still valid species. The latter was described by Jöns Berzelius in 1829 and from this material Berzelius isolated and described the new element thorium (Berzelius, 1829). Hausmann (1813) gave the name *esmarkite* specifically to datolite from the Arendal iron mines in Norway, to honour Jens Esmark, who discovered datolite. Berzelius named a mineral *esmarkite* after H. M. T. Esmark, but it was later shown to be a hydrous cordierite (Erdmann, 1840). To avoid confusion with the two different *esmarkite* names in the literature and to emphasize that the mineral is named after H. M. T. Esmark and not his father, the name *hansesmarkite* was chosen for this new niobate.

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-067, Friis *et al.*, 2015). Single-crystal and electron probe microanalyses (EPMA) data were collected on crystals from one sample (catalogue number 43584) stored at the Natural History Museum, University of Oslo. The epoxy mount used for EPMA has catalogue number 43585. The sample from which crystals for optical work was used has catalogue number 43586. The crystal used for structure solution was lost. A vial containing loose crystals (from sample 43586, of the Natural History Museum in Oslo) is in the collections of the Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number 64165.

Occurrence

The LPC is the southernmost magmatic event of the Carboniferous to Permian Oslo rift system and consists of ten intrusive ring sections (Fig. 1) (Petersen, 1978). The alkalinity of the rocks and

pegmatites generally increases from ring sections 1 through to 10 (Petersen, 1978; Dahlgren, 2010). The AS Granit quarry in Tvedalen, Larvik, Vestfold, Norway (WGS 84 GPS coordinates: N 59° 2.353', E 9° 51.413') is situated within ring section 6 (Fig. 1). Hanesmarkite was discovered in a miaskitic pegmatite dyke on level 4 of the AS Granit larvikite quarry. The dyke was up to 20 cm thick and dipped 30° to the south. It was later blasted and completely removed during on-going quarrying activity. Hanesmarkite occurs on fracture surfaces in the centre of the dyke and always on top of gonnardite. The primary minerals of the pegmatite are annite, amphibole (hastingsite group), magnetite, grey microcline, greenish nepheline (partly altered to natrolite 'spreustein'), pyrochlore, thorite, wöhlerite and zircon. The part of the pegmatite dyke in which hanesmarkite occurred experienced hydrothermal alteration, yielding the following mineral assemblage: analcime, arsenopyrite, behoite, bertrandite, calcite, chiavennite, chlorite, epididymite, fluorapophyllite-(K), fluorite, galena, gonnardite, hambergite, luinaite-(OH), molybdenite, natrolite, neotocite, peterandresenite and hanesmarkite.

Physical and optical properties

Hanesmarkite typically occurs as fine-grained material in well-defined patches up to 6 mm across (Fig. 2). Distinct crystals, as elongated tablets up to 0.3 mm long, occur rarely within the patches. Crystals are elongated on [100] and exhibit the forms {100}, {010}, {011}, {01 $\bar{1}$ }, {10 $\bar{1}$ }, {1 $\bar{1}$ 1}, {1 $\bar{1}$ 0}, {122}, {12 $\bar{3}$ } and {210} (Fig. 3).



FIG. 2. Photomicrograph of a patch (6 mm across) containing yellow hanesmarkite and orange peterandresenite along the edge and outside the patch. The white matrix is gonnardite.

Hanesmarkite is yellow with a very pale yellow streak. Crystals are transparent and have a vitreous to resinous lustre. Hanesmarkite exhibits no luminescence under longwave or shortwave ultraviolet light or under exposure to an electron beam. The Mohs hardness was not determined, but is probably 2–2½, based on the similarity of the mineral to peterandresenite. The tenacity is brittle and the fracture is curved. Crystals exhibit good cleavage on {011} and {01 $\bar{1}$ }. Because of the very limited amount of material available, the density was not determined experimentally, but based on the empirical formula and unit-cell parameters at room temperature, it was calculated to be 2.74 g cm⁻³ for the empirical formula and 2.76 g cm⁻³ for the ideal formula.

Optically, hanesmarkite is biaxial (+), with $\alpha = 1.683(2)$, $\beta = 1.698(2)$ and $\gamma = 1.745(3)$ measured in white light. The 2V measured from extinction data using *EXCALIBUR* (Gunter *et al.*, 2004) is 60.7(6)° and the calculated 2V is 60.3°. The mineral exhibits moderate $r > v$ dispersion and is pleochroic with X (almost colourless) $< Y$ (pale yellow) $\ll Z$ (orange yellow). The optical orientation is $X \wedge c = 20^\circ$, $Y \wedge b = 16^\circ$ and $Z \wedge a = 5^\circ$. The Gladstone-Dale compatibility index, $1 - (K_p/K_c)$, is -0.043, i.e. good (Mandarino, 1981).

Composition

The chemical analyses of hanesmarkite were performed in wavelength-dispersive mode on a

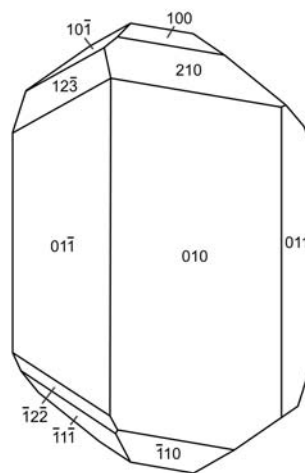


FIG. 3. Crystal drawing of hanesmarkite (clinographic projection in non-standard orientation).

TABLE 1. Chemical composition of five analyses and formula of hansemarkite based on Nb = 6 and the required composition for the ideal formula.

	Hansemarkite		Ideal Wt.%
	Wt.%	apfu	
Nb ₂ O ₅	64(1)	6	56.48
MnO	10.2(3)	1.79	10.05
CaO	8.6(3)	1.93	7.94
FeO	0.6(3)	0.11	
Na ₂ O	0.04(3)	0.02	
K ₂ O	0.02(2)	0.01	
H ₂ O*	28.94	20	25.52
Total	112.6		100

*Based on stoichiometry and structure; apfu – atoms per formula unit.

CAMECA SX-100 electron microprobe housed in the Department of Geosciences, University of Oslo using an acceleration voltage of 15 kV, a current of 6 nA and a beam diameter of 10 µm. The intensity data were corrected for inter-element overlaps and matrix effects using a Cameca version of the ‘PAP-φρz’ routine (Pouchou and Pichoir, 1984). The following standards were used: albite (Na), microcline (K), pure metal (Nb, Fe), pyrophanite (Mn) and wollastonite (Ca). A Hitachi S-3600 low vacuum scanning electron microscope (SEM) equipped with a Bruker Xflash 5030 energy-dispersive X-ray spectrometry (EDS) detector was used to check for other elements than those sought for by EPMA, but none were found. The results of five EPMA analyses are given in Table 1. There is a rather large discrepancy between the content of Nb and H₂O from the EPMA analysis compared to the expected values from the ideal composition. The main reason being that hansemarkite, like peterandresenite, readily dehydrates in a vacuum, hence the majority of water has already been lost during the coating process. Therefore the resulting EPMA data will show abnormal high element concentrations causing high totals. Hansemarkite is extremely prone to dehydration. In one single-crystal X-ray diffraction experiment, when air flowed over the crystal it deteriorated in a matter of hours resulting in broadening and striation of reflections. The EDS was carried out in a low vacuum SEM, but the dehydration had already occurred by the time a beam could be applied, and was visible by the formation of cracks in the mineral such as those

observed for peterandresenite (Friis *et al.*, 2014). Furthermore, when the sample was removed from the SEM it had turned milky, indicating a significant compositional change. Therefore, wet chemical analysis would be the only way to acquire accurate compositional data, but insufficient material existed for such analyses. The empirical formula was calculated based on Nb = 6 atoms per formula unit and water content from the structure solution to (Ca_{1.93}Na_{0.02}K_{0.01})_{Σ1.96}(Mn_{1.79}Fe_{0.11})_{Σ1.90}Nb₆O_{18.84}·20H₂O. The ideal formula of Ca₂Mn₂Nb₆O₁₉·20H₂O, which requires Nb₂O₅ 56.48, MnO 10.05, CaO 7.94, H₂O 25.52, total 100 wt.%.

Raman spectroscopy

The Raman spectrum was obtained using a Renishaw inVia Raman Microscope equipped with a 532 nm laser housed at the Microscopy and Analysis Suite (MAS), University of Bath. The peak positions and shapes were modelled using the Renishaw *WIRE* software. Hansemarkite slowly lost water during the experiments, resulting in broadening of the peaks. The observed Raman bands and their assignments are listed in Table 2. All bands are associated with the Lindqvist ion and are typical for such compounds (e.g. Farrell *et al.*, 1969; Jehng and Wachs, 1991).

Crystallography

Single crystal X-ray diffraction intensity data were collected at 120 K at the Department of Chemistry, University of Southampton on a Rigaku FR-E+ SuperBright equipped with a Saturn 724+ CCD detector using monochromatized MoK α radiation. The structure was solved by direct methods (Sheldrick, 2008) using neutral-atom scattering factors. After all non-hydrogen atoms were located, anisotropic displacement factors were applied and the structure refined with *SHELXL* using the *WinGX* interface (Farrugia, 2012). The difference-Fourier syntheses provided all hydrogen atom positions, which all refined with meaningful O–H distances. The occupancies of the major cations were released one by one, but did not vary significantly from full occupancy; consequently, all sites were assigned full occupancy in the final refinements. Table 3 provides details of the data collection and refinement and Table 4 the fractional coordinates and anisotropic displacement parameters. Selected bond distances are presented in Table 5 and the hydrogen bonding scheme in

TABLE 2. Observed Raman bands and their assignment in hanesmarkite.

Band (cm ⁻¹)	Intensity and shape	Band assignment*
913	Strong and narrow	Stretching of Nb– <i>Or</i>
865	Medium and narrow	Stretching of Nb– <i>Or</i>
841	Weak shoulder	Stretching of Nb– <i>Or</i>
734	Weak and broad	Stretching of Nb– <i>Ob</i>
520	Weak and broad	Stretching of Nb– <i>Ob</i> /Breathing mode <i>Ob</i>
473	Weak shoulder	Stretching of Nb– <i>Ob</i> /Breathing mode <i>Ob</i>
302	Medium narrow	Nb–O–Nb cage deformation
217	Medium narrow	Nb–O–Nb bending mode

* Assignments are based on published hexaniobates especially Farrell *et al.* (1969) and Jehng and Wachs (1991)

Table 6. One data collection was also performed at room temperature, resulting in the following unit-cell parameters: $a = 9.081(4)$, $b = 9.982(8)$, $c = 10.60(1)$ Å, $\alpha = 111.07(8)$, $\beta = 101.15(6)$, $\gamma = 99.39(5)^\circ$ and $V = 850.8(13)$ Å³. However, the structure determined from the room temperature data did not refine as well as that obtained using the 120 K dataset, and it was not possible to locate all

hydrogen atoms. Therefore, the room-temperature data were only used for: (1) the calculated powder X-ray diffraction data; (2) the calculated density; and (3) the Gladstone-Dale compatibility index. The structure refinement is based on the low-temperature data.

Six NbO₆ octahedra (three independent Nb sites) share edges to form the ‘super octahedron’ referred to as the Lindqvist ion (Lindqvist, 1953). The MnO₄(H₂O)₂ octahedron is connected via edge-sharing to each of the three independent Nb octahedra in the Lindqvist ion in a *trans* configuration, i.e. attached to opposite faces of the super octahedron. Each Mn octahedron shares three bridging O atoms (*Ob*) with one Lindqvist ion, i.e. oxygens that bond to two Nb-atoms, and one terminal O atom (*Or*), i.e. an oxygen that only bonds to one Nb-atom, with the Nb2 octahedron of the adjacent Lindqvist ion, creating a rod of Lindqvist ions and Mn octahedra along [100] (Fig. 4). The two remaining O atoms of the Mn octahedron are H₂O groups. Calcium is in a distorted seven coordination, only bonding to the *Or* of the Nb3 octahedron and occupying the space between the rods (Fig. 5). The remaining six O atoms of the Ca-coordination are all H₂O groups. In addition to the water connected to the Mn and Ca-coordinations, two isolated H₂O groups are located between the rods. The rods are linked into a three-dimensional structure via hydrogen bonds, especially from the six terminal O atoms of the Ca-coordination.

The Nb–O bond distances in each octahedron include: one short Nb–O bond (<Nb–O> = 1.777 Å), four intermediate Nb–O bonds (<Nb–O> = 1.997 Å) and one long Nb–O bond (<Nb–O> = 2.377 Å). The short distances (Nb2–O7 = 1.766 and Nb3–O10 = 1.785 Å) correspond to the O

TABLE 3. Single-crystal data collection and results.

Space group	$P\bar{1}$
Temperature (K)	120(2)
a (Å)	9.031(3)
b (Å)	9.917(4)
c (Å)	10.684(4)
α (°)	112.828(6)
β (°)	101.050(4)
γ (°)	98.879(4)
V (Å ³)	837.5(5)
Z	1
$2\theta_{\max}$ (°)	69.22
Total reflections	13,825
Unique reflections	6537
R_{int} (%)	1.92
R_{σ} (%)	3.26
$R1$ for $F_o > 4\sigma$ (%)	2.50
$R1_{\text{all}}$ (%)	3.10
$wR2$ (%)	4.81
Goof	1.066
i	0.0207
j	0.03
Residuals ($e/\text{Å}^3$)	+0.980/–0.933

$$R1 = \frac{\sum (F_o - F_c)}{\sum F_o}$$

$$w = 1/(\sigma^2(F_o^2) + (i * P)^2 + j * P) \text{ where } P = (\max. (F_o^2, 0) + 2F_c^2)/3.$$

$$wR2 = [(\sum w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}.$$

TABLE 4. Fractional atom coordinates and thermal parameters (\AA^2) for hanesmarkite at 120 K.

	x	y	x	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nb1	0.44938(2)	0.39083(2)	0.65721(2)	0.00412(3)	0.00433(6)	0.00415(6)	0.00455(7)	0.00246(5)	0.00125(5)	0.00133(5)
Nb2	0.72334(2)	0.40483(2)	0.49167(2)	0.00398(3)	0.00374(6)	0.00361(6)	0.00492(7)	0.00196(5)	0.00130(5)	0.00139(5)
Nb3	0.64787(2)	0.72570(2)	0.70073(2)	0.00402(3)	0.00411(6)	0.00342(6)	0.00413(7)	0.00130(5)	0.00102(5)	0.00088(5)
Mn	0.09389(3)	0.26788(3)	0.46810(3)	0.00542(5)	0.00421(6)	0.00531(1)	0.00731(1)	0.00291(1)	0.00214(9)	0.00165(8)
Ca	0.75343(4)	0.15895(4)	0.95750(4)	0.00622(6)	0.00681(1)	0.00561(1)	0.00602(2)	0.00231(1)	0.00141(1)	0.00171(1)
O1	0.5	0.5	0.5	0.0057(3)	0.0054(7)	0.0057(7)	0.0069(8)	0.0032(7)	0.0017(6)	0.0021(6)
O2	0.4068(1)	0.3072(1)	0.7708(1)	0.0081(2)	0.0085(5)	0.0087(5)	0.0091(6)	0.0051(5)	0.0037(5)	0.0027(4)
O3	0.5770(1)	0.5954(1)	0.7871(1)	0.0061(2)	0.0073(5)	0.0055(5)	0.0050(6)	0.0018(5)	0.0020(4)	0.0009(4)
O4	0.6403(1)	0.3312(1)	0.6182(1)	0.0065(2)	0.0068(5)	0.0070(5)	0.0075(6)	0.0044(5)	0.0022(4)	0.0029(4)
O5	0.2663(1)	0.4804(1)	0.6290(1)	0.0057(2)	0.0057(5)	0.0056(5)	0.0064(6)	0.0026(5)	0.0025(4)	0.0024(4)
O6	0.3261(1)	0.2255(1)	0.4631(1)	0.0055(2)	0.0051(5)	0.0048(5)	0.0065(6)	0.0023(5)	0.0016(4)	0.0011(4)
O7	0.8939(1)	0.3396(1)	0.4816(1)	0.0076(2)	0.0069(5)	0.0076(5)	0.0109(7)	0.0047(5)	0.0043(5)	0.0043(4)
O8	0.5623(1)	0.2370(1)	0.3297(1)	0.0061(2)	0.0062(5)	0.0057(5)	0.0063(6)	0.0022(5)	0.0016(4)	0.0020(4)
O9	0.8114(1)	0.6133(1)	0.6528(1)	0.0059(2)	0.0055(5)	0.0059(5)	0.0065(6)	0.0029(5)	0.0015(4)	0.0015(4)
O10	0.7553(1)	0.8985(1)	0.8493(1)	0.0077(2)	0.0079(5)	0.0055(5)	0.0083(6)	0.0018(5)	0.0021(4)	0.0007(4)
O11	0.0479(2)	0.1731(2)	0.6109(2)	0.0111(3)	0.0112(6)	0.0111(6)	0.0123(7)	0.0070(5)	0.0020(5)	0.0020(5)
O12	0.9571(2)	0.0627(2)	0.2823(2)	0.0102(3)	0.0092(6)	0.0115(6)	0.0087(7)	0.0025(5)	0.0022(5)	0.0047(5)
O13	0.8876(2)	0.3657(2)	0.1790(2)	0.0105(3)	0.0091(6)	0.0121(6)	0.0067(7)	0.0004(5)	0.0007(5)	0.0039(5)
O14	0.8192(2)	0.3441(2)	0.8715(2)	0.0118(3)	0.0151(6)	0.0102(6)	0.0099(7)	0.0056(6)	0.0006(5)	0.0027(5)
O15	0.0240(2)	0.1583(2)	0.9705(2)	0.0097(3)	0.0078(5)	0.0084(6)	0.0120(7)	0.0047(5)	0.0008(5)	0.0013(4)
O16	0.5192(2)	0.2427(2)	0.9913(2)	0.0103(3)	0.0135(6)	0.0119(6)	0.0082(7)	0.0047(5)	0.0054(5)	0.0069(5)
O17	0.5603(2)	0.0629(2)	0.7292(2)	0.0098(3)	0.0099(6)	0.0070(6)	0.0111(7)	0.0034(5)	0.0009(5)	0.0023(5)
O18	0.6762(2)	0.0596(2)	0.1199(2)	0.0094(3)	0.0108(6)	0.0074(6)	0.0100(7)	0.0028(5)	0.0051(5)	0.0022(5)
O19	0.1729(2)	0.3802(2)	0.9161(2)	0.0144(3)	0.0142(6)	0.0139(7)	0.0155(8)	0.0061(6)	0.0058(6)	0.0028(5)
O20	0.7433(2)	0.0464(2)	0.5179(2)	0.0128(3)	0.0148(6)	0.0085(6)	0.0177(8)	0.0069(6)	0.0077(5)	0.0030(5)
H1	0.093(4)	0.119(4)	0.638(4)		0.05(1)					
H2	0.943(3)	0.127(3)	0.587(3)		0.033(8)					
H3	0.992(3)	0.012(3)	0.217(3)		0.038(9)					
H4	0.871(4)	0.070(3)	0.241(3)		0.04(1)					
H5	0.976(3)	0.379(3)	0.223(3)		0.020(7)					
H6	0.849(3)	0.416(3)	0.233(3)		0.013(6)					
H7	0.774(3)	0.337(3)	0.794(3)		0.018(7)					
H8	0.821(3)	0.423(3)	0.921(3)		0.033(8)					
H9	0.082(3)	0.140(2)	0.028(2)		0.010(6)					
H10	0.069(3)	0.221(3)	0.960(3)		0.034(9)					
H11	0.488(3)	0.279(3)	0.933(3)		0.033(8)					

HANSESMARKITE, A NEW HEXANIOPATE FROM NORWAY

TABLE 5. Selected bond distances (Å) in hanesmarkite at 120 K.

Nb1–O2	1.780(1)	Mn–O7	2.050(1)
Nb1–O3	1.962(1)	Mn–O11	2.149(2)
Nb1–O4	1.973(1)	Mn–O12	2.180(2)
Nb1–O5	2.020(1)	Mn–O6	2.208(1)
Nb1–O6	2.034(1)	Mn–O5	2.230(1)
Nb1–O1	2.3990(6)	Mn–O9	2.254(1)
Mean	2.028	Mean	2.178
Nb2–O7	1.766(1)	Ca–O13	2.375(2)
Nb2–O4	1.977(1)	Ca–O10	2.389(2)
Nb2–O8	1.982(1)	Ca–O14	2.398(2)
Nb2–O9	2.019(1)	Ca–O15	2.422(2)
Nb2–O5	2.029(1)	Ca–O16	2.428(2)
Nb2–O1	2.3576(6)	Ca–O17	2.438(2)
Mean	2.021	Ca–O18	2.459(2)
		Mean	2.415
Nb3–O10	1.785(1)		
Nb3–O3	1.956(1)		
Nb3–O8	1.979(1)		
Nb3–O9	2.010(1)		
Nb3–O6	2.033(1)		
Nb3–O1	2.3764(6)		
Mean	2.023		

H12	0.498(3)	0.293(3)	0.058(3)	0.027(8)
H13	0.502(3)	0.110(3)	0.719(3)	0.042(9)
H14	0.506(3)	0.983(3)	0.695(3)	0.032(8)
H15	0.625(4)	0.983(4)	0.089(3)	0.04(1)
H16	0.642(3)	0.115(3)	0.175(3)	0.039(9)
H17	0.251(4)	0.368(3)	0.893(3)	0.035(9)
H18	0.106(4)	0.367(4)	0.848(4)	0.05(1)
H19	0.717(3)	0.980(3)	0.536(3)	0.020(7)
H20	0.690(4)	0.108(4)	0.549(4)	0.05(1)

TABLE 6. Hydrogen bonds in hanesmarkite at 120 K.

D–H...A	D–H	H...A	D...A	<DHA
O11–H1...O12	0.83(4)	2.30(4)	2.972(3)	140(3)
O11–H2...O20	0.93(3)	1.74(3)	2.655(2)	171(3)
O12–H3...O15	0.83(3)	2.02(3)	2.798(2)	154(3)
O12–H4...O18	0.85(3)	1.94(3)	2.774(2)	171(3)
O13–H5...O9	0.81(3)	2.09(3)	2.884(2)	170(3)
O13–H6...O5	0.78(3)	2.01(3)	2.790(2)	172(3)
O14–H7...O4	0.82(3)	2.00(3)	2.818(2)	172(3)
O14–H8...O19	0.75(3)	2.03(3)	2.773(3)	169(3)
O15–H9...O10	0.82(2)	1.96(2)	2.777(2)	171(2)
O15–H10...O19	0.75(3)	1.97(3)	2.714(3)	174(3)
O16–H11...O2	0.86(3)	1.89(3)	2.729(2)	166(3)
O16–H12...O3	0.77(3)	1.92(3)	2.683(2)	174(3)
O17–H13...O2	0.78(3)	2.18(3)	2.903(2)	157(3)
O17–H14...O8	0.77(3)	2.07(3)	2.782(2)	154(3)
O18–H15...O16	0.73(4)	2.15(4)	2.884(3)	177(3)
O18–H16...O8	0.78(3)	1.97(3)	2.750(2)	172(3)
O19–H17...O2	0.80(4)	2.10(3)	2.873(2)	162(3)
O19–H18...O11	0.80(4)	2.41(4)	2.967(2)	128(3)
O20–H19...O6	0.77(3)	2.02(3)	2.768(2)	163(3)
O20–H20...O4	0.84(4)	2.19(4)	2.973(2)	154(4)
O20–H20...O17	0.84(4)	2.58(4)	3.013(2)	113(3)

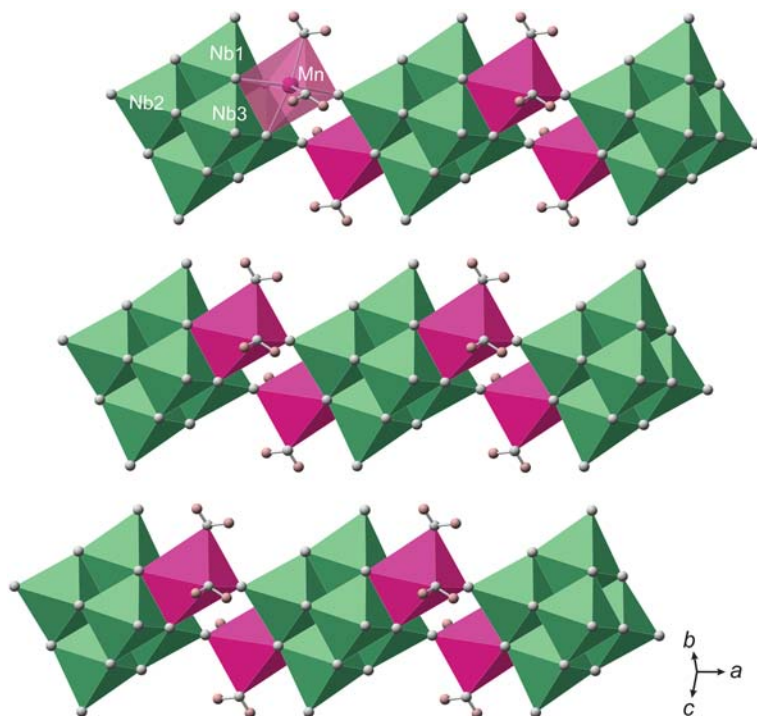


FIG. 4. A view perpendicular to the a axis showing how the Mn^{2+} octahedra (pink) tie the Lindqvist ions (green) into rods along $[100]$. The terminal oxygen atoms of the Mn octahedron bond to hydrogen (faint pink). Calcium ions and water molecules coordinated to calcium and non-bonded atoms have been excluded for simplicity. Generated using *CrystalMaker*®.

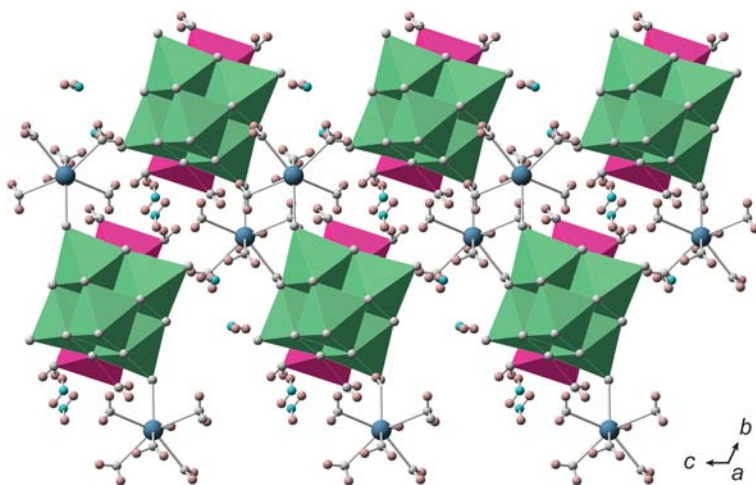


FIG. 5. A view along the a axis showing how the seven-coordinated Ca (blue) ion only connects to one Lindqvist ion and fills the space between the rods tying the structure together via hydrogen bonds. For simplicity some Ca-coordinations have been removed from the lower part of the figure. The turquoise atoms represent the non-coordinated water molecules and the faint pink atoms are hydrogen. Generated using *CrystalMaker*®.

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TABLE 7. Bond-valence analysis of hanesmarkite at 120 K.

	Nb1	Nb2	Nb3	Mn	Ca	H bonds	Σ
O1	0.27 2x→	0.30 2x→	0.28 2x→				1.70
O2	1.42					0.10; 0.08; 0.09	1.69
O3	0.87		0.89			0.11	1.87
O4	0.85	0.84				0.09; 0.08	1.86
O5	0.74	0.73		0.30		0.09	1.86
O6	0.72		0.72	0.32		0.10	1.86
O7		1.48		0.50			1.98
O8		0.83	0.83			0.09; 0.10	1.85
O9		0.75	0.77	0.29		0.09	1.90
O10			1.41		0.32	0.10	1.83
O11				0.38		0.76; 0.68; 0.08	1.90
O12				0.35		0.76; 0.74; 0.08	1.93
O13					0.33	0.77; 0.80	1.90
O14					0.31	0.77; 0.82	1.90
O15					0.29	0.77; 0.82; 0.09	1.97
O16					0.29	0.73; 0.81; 0.09	1.92
O17					0.28	0.80; 0.81; 0.07	1.96
O18					0.26	0.84; 0.80; 0.10	2.00
O19						0.78; 0.78; 0.10; 0.10	1.76
O20						0.81; 0.75; 0.11	1.67
Σ	4.87	4.93	4.90	2.14	2.08		

Note: Values are expressed in valance units (vu). Bond strengths calculated from Brese and O'Keeffe (1991) and in the case of hydrogen from Brown (2002).

→ indicates two bonds due to symmetry.

atoms that are corner connected to the Mn and Ca coordinations, respectively. In the Nb1 octahedron, the shortest distance is to the terminal O2, which does not bond to any other cations. The intermediate bond-distances are to O atoms, which are bridging two Nb sites, whereas the long distances are to the central oxygen (O1) of the Lindqvist ion. The Nb–O bond distances in hanesmarkite are similar to those observed in peterandresenite and melcherite (Friis *et al.*, 2014; Andrade *et al.*, 2015). The average Mn–O bond distance in hanesmarkite is 2.178 Å, compared to 2.222 Å for the similar Mn1 site in peterandresenite. Furthermore, the difference between shortest and longest Mn–O distance is only 0.204 Å, compared to 0.261 Å in the distorted Mn1 octahedron in peterandresenite. The bond lengths of the seven-coordinated Ca site only show minor variations (over a range of 0.084 Å) with an average of 2.415 Å.

A summary of the bond-valence calculations is provided in Table 7. The bond-valence sums (BVS) for all Nb sites are slightly below the ideal five and for Mn it is just above two, whereas for Ca it is the ideal two. The bond-valence analysis confirms that the Mn is divalent.

Powder XRD

Traditional powder X-ray diffraction (PXRD) could not be collected due to the small amount of material available and the fact that hanesmarkite was almost impossible to separate from the gonnardite matrix. A simulated PXRD was collected at room temperature on a small crystal fragment with an Agilent Supernova, dual tube Eos S2 diffractometer using MoK α radiation housed at the Department of Chemistry, University of Bath, UK. The experimental PXRD intensities and *d* values are given in Table 8 with calculated values produced with *CrystalDiffract*® from the room temperature refinement. There is a good agreement between the experimental and calculated values, although a small offset is observed.

Comparison with other structures

Hanesmarkite is only the third natural hexaniobate to be described and is chemically most closely related to peterandresenite (see Table 9). The Mn octahedron in hanesmarkite and the Mn1 octahedron in peterandresenite both connect adjacent

TABLE 8. Observed and calculated intensities and *d* values (Å) for hansesmarkite from simulated powder XRD and structure refinement at room temperature.

<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>h k l</i>	<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>h k l</i>
36	9.282	9.515	94	0 0 1					
100	8.610	{ 8.615 8.464	{ 31 100	{ 1 0 0 0 1 $\bar{1}$	6	2.456	{ 2.468 2.466 2.461	{ 1 2 1	{ 2 $\bar{1}$ 3 1 $\bar{4}$ 1 2 3 $\bar{2}$
6	7.414	7.484	18	1 0 $\bar{1}$	3	2.193	{ 2.174 2.169	{ 4 8	{ 0 3 2 4 $\bar{2}$ 0
14	7.108	7.204	30	1 $\bar{1}$ 0					
5	6.043	6.024	15	1 $\bar{1}$ 1	5	2.136	2.153	6	4 2 1
12	5.412	5.520	14	0 1 1	2	2.113	2.118	2	0 4 4
9	4.467	4.505	9	0 2 0					
2	4.310	{ 4.340 4.308	{ 1 1	{ 2 $\bar{1}$ 0 2 0 0	6	2.083	{ 2.079 2.067 2.059	{ 1 1 3	{ 4 $\bar{2}$ 1 2 4 1 1 4 4
8	4.165	4.155	9	1 $\bar{1}$ 2	6	2.037	2.050	2	2 2 2
2	3.999	4.074	2	2 $\bar{1}$ 1					
2	3.572	{ 3.583 3.574	{ 1 1	{ 2 1 $\bar{2}$ 2 0 1	4	1.973	{ 2.009 1.993	{ 11 7	{ 4 3 0 1 2 3
3	3.486	3.551	3	2 1 0	3	1.875	{ 1.890 1.870	{ 1 2	{ 4 2 $\bar{3}$ 4 1 4
30	3.257	{ 3.267 3.259	{ 9 11	{ 0 3 $\bar{1}$ 1 $\bar{3}$ 1	7	1.819	{ 1.822 1.788	{ 2 3	{ 4 1 1 4 0 2
7	3.104	3.184	8	1 2 $\bar{3}$					
18	3.058	{ 3.090 3.084	{ 8 8	{ 1 $\bar{3}$ 0 2 $\bar{1}$ 2	7	1.734	{ 1.770 1.725 1.723	{ 2 2 1	{ 3 4 2 5 0 $\bar{3}$ 3 1 5
		{ 2.985 2.982	{ 3 14	{ 3 0 $\bar{1}$ 1 2 1	3	1.693	{ 1.720 1.689	{ 3 4	{ 2 5 4 2 5 $\bar{2}$
9	2.980	{ 2.980 2.973 2.963	{ 3 6 8	{ 1 2 3 2 0 $\bar{3}$ 3 $\bar{1}$ 0	2	1.665	{ 1.683 1.649 1.646	{ 3 2 2	{ 0 1 $\bar{6}$ 1 3 4 3 5 1
		{ 2.760 2.750	{ 4 3	{ 3 2 0 2 2 2	5	1.605	{ 1.623 1.620	{ 2 2	{ 5 0 4 5 0 1
17	2.715	{ 2.743 2.724	{ 2 6	{ 1 0 3 3 1 $\bar{1}$	6	1.499	{ 1.501 1.498 1.495	{ 2 1 4	{ 0 6 0 5 0 5 3 1 4
7	2.650	{ 2.688 2.686	{ 3 11	{ 3 1 $\bar{2}$ 1 3 $\bar{3}$					
		{ 2.666 2.662	{ 2 5	{ 2 1 3 3 2 1	5	1.452	{ 1.468 1.465	{ 1 2	{ 5 3 3 2 6 3
12	2.628	2.640	4	3 2 1					

Lindqvist ions; however, in peterandresenite, each Mn1 octahedron connects three Lindqvist ions, creating a two-dimensional layer. In contrast, the Mn octahedron in hansesmarkite only connects two Lindqvist ions, resulting in the formation of a rod, rather than a layer. In melcherite, the large Ba-coordination links, via edge-sharing, three Lindqvist ions, forming two-dimensional layers perpendicular to the *c* axis. The layers are connected by direct bonding via the Ca-coordination, which shares edges with three Nb octahedra of one Lindqvist ion and shares corners with three Lindqvist ions in the adjacent layer. In peterandresenite, the adjacent Lindqvist-Mn1 layers are slightly offset in the *ab*-plane and the

Mn2 octahedron protrudes into the space between adjacent layers, and the structure is held together in three dimensions by hydrogen bonding. In hansesmarkite, it is the seven-coordinated Ca site that occupies the space between the rods and creates the three-dimensional structure purely through hydrogen bonds. The major structural difference between the three hexaniobate minerals is that, in melcherite, the three-dimensional structure is achieved via direct bonding between the Lindqvist ions and the other cation coordinations, whereas in hansesmarkite and peterandresenite, the three-dimensional structure is accomplished by hydrogen bonding.

The connectivity between the Lindqvist ions in peterandresenite has not been observed before in

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TABLE 9. Comparison of hanesmarkite with other natural hexaniobates.

	Hanesmarkite	Peterandresenite ¹	Melcherite ²
Formula	Ca ₂ Mn ₂ Nb ₆ O ₁₉ ·20H ₂ O	Mn ₄ Nb ₆ O ₁₉ ·14H ₂ O	(Ba,K) ₂ (Na,Ca) ₂ Mg Nb ₆ O ₁₉ ·6H ₂ O
Space group	<i>P</i> $\bar{1}$	<i>C2/m</i>	<i>R</i> 3
<i>a</i> (Å)	9.081(4)	15.329(1)	9.0117(6)
<i>b</i> (Å)	9.982(8)	9.4121(5)	
<i>c</i> (Å)	10.60(1)	11.2832(9)	23.3986(16)
α (°)	111.07(8)		
β (°)	101.15(6)	118.650(4)	
γ (°)	99.39(5)		
<i>Z</i>	1	2	3
<i>V</i> (Å ³)	851.5(13)	1428.6(2)	1645.64(19)
Strongest	8.610 (100)	2.9260 (100)	7.805 (100)
PXRD lines	9.282 (36)	9.8977 (82)	3.250 (33)
\bar{d} (Å)	3.257 (30)	7.1026 (63)	2.165 (30)
Optics	Biaxial (+)	Biaxial (–)	Uniaxial (?)

1: Friis *et al.* (2014); 2: Andrade *et al.* (2015).

synthetic compounds. However, the linear connectivity in hanesmarkite is similar to what has been described in Rb₂[Cu(NH₃)₂(H₂O)₄][Cu(NH₃)₄(H₂O)₂]₂{[Nb₆O₁₉][Cu(NH₃)₂]₂·6H₂O} (henceforth referred to as Bon3), which also crystallizes in *P* $\bar{1}$ (Bontchev *et al.*, 2007). In Bon3, it is Cu²⁺ that bonds to two *Ob* of one Lindqvist and one *Ot* of the adjacent Lindqvist ion resulting in a rod-structure similar to that of hanesmarkite. Although Bontchev *et al.* (2007) described the connection between the hexaniobates as a planar coordination of Cu²⁺ with three oxygens and one NH₃-group, a third *Ob* is only 2.4 Å away, indicating that Cu is five-coordinated rather than four-coordinated. Ma *et al.* (2011) described such a five-coordination for Cu in a similar rod-hexaniobate. Bond-valence calculations indicate that Cu would be five- rather than four-coordinated. Hence, the connectivity between Lindqvist ions in hanesmarkite and in the two synthetic compounds is the same.

Origin of hanesmarkite

The pegmatite hosting hanesmarkite contained partly altered pyrochlore, which is likely to be the source of Nb and Ca. The origin of Mn is not as easily explained, but it is typical for the late-stage phases in the pegmatites to contain Mn, e.g. chiavennite (CaMnBe₂Si₅O₁₃(OH)₂·2H₂O). The vein also contained neotocite, (Mn,Fe,Mg)SiO₃·H₂O, indicating a Mn-rich alteration event. Although the

alteration of primary wöhlerite could provide some Mn, it would not be sufficient to explain the Mn-enrichment in the late hydrothermal stage. Neotocite often forms a coating on the host pegmatite, and is deposited prior to the formation of chiavennite and the hexaniobates. The hexaniobates are the last minerals to form. Therefore, it is possible that some of the neotocite was dissolved by the fluids that dissolved the pyrochlore and, hence, could provide a source for the Mn. An alternative explanation is that highly etched rhodochrosite, which was observed in some pegmatites on a higher level in the quarry, could have been the source of the Mn. Currently, it is not possible to establish which of these candidates is the most likely source of the Mn in the hexaniobates.

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