The Canadian Mineralogist
Vol. 49, pp. 595-604 (2011)
DOI: 10.3749/canmin.49.2.595

RAKOVANITE, $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$, A NEW MEMBER OF THE PASCOITE FAMILY WITH A PROTONATED DECAVANADATE POLYANION

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ABSTRACT

Rakovanite, $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$, is a new mineral species from the Sunday and the West Sunday mines, Slick Rock district, San Miguel County, Colorado, USA; the mineral is the natural analog of the previously synthesized phase. Rakovanite is orange, with an orange-yellow streak. Crystals of rakovanite are up to 1 mm in maximum dimension and vary in habit from blocky to prismatic on [100]. The mineral is transparent, with a subadamantine luster; it does not fluoresce in long- or short-wave ultraviolet radiation. Rakovanite displays brittle tenacity, and has a Mohs hardness of 1. No cleavage or parting was observed, and the mineral displays a conchoidal fracture. The density calculated from the ideal formula and the single-crystal cell data is 2.407 g cm^{-3}. Rakovanite is biaxial (+), with α_{589nm} = 1.776(5), β_{589nm} = 1.803(5), γ_{589nm} = 1.910(6). The measured values of $2V$ are: $2Vz_{540nm}$ = 58(1); $2Vz_{589nm}$ = 56(1); $2Vz_{650nm}$ = 53(1)°. Dispersion is $r < v$, strong, parallel; orientation: $X = \mathbf{b}$; $Z \wedge \mathbf{c} = 8°$ in obtuse β. The pleochroic scheme in rakovanite is: X light yellow, Y orangish yellow, Z yellowish orange, $Z > Y > X$. Its chemical composition was obtained by electron-probe microanalysis and the crystal-structure refinement; the empirical formula (V = 10 *apfu*) is $(Na_{2.90}K_{0.07}Ca_{0.01}Al_{0.01})_{\Sigma 2.99}\{H_{2.98}[V_{10}O_{28}]\}\bullet 15H_2O$, and the simplified formula is $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$. Rakovanite is monoclinic, space group $P2_1/n$, with a 12.0248(17), b 17.121(3), c 18.140(3) Å, β 106.242(8)°, and Z = 4; the strongest four lines in the powder-diffraction pattern [d in Å(I)(hkl)] are: 11.270(100)($\bar{1}01$), 7.696(81)(021), 8.709(78)(002), and 6.892(63)(120). The atomic arrangement of rakovanite has been refined to R_1 = 0.0383; the structural unit in the phase is formed of a triply-protonated decavanadate polyanion, $\{H_3[V_{10}O_{28}]\}$. The structural units are linked by the interstitial complexes, the $(Na_3\bullet 15H_2O)$ contents of which balance the +3 charges of the decavanadate polyanion with a $NaO_4(H_2O)_2$ group, a $Na_2(H_2O)_{10}$ dimer, and three H_2O molecules that do not bond to the interstitial cations.

Keywords: rakovanite, new mineral species, decavanadate, crystal structure, Sunday and West Sunday mines, Slick Rock district, Colorado.

SOMMAIRE

La rakovanite, $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$, est une nouvelle espèce minérale découverte aux mines Sunday et West Sunday, district de Slick Rock, comté de San Miguel, au Colorado; c'est l'analogue naturel d'une phase synthétique déjà caractérisée. La rakovanite est orange, avec une rayure orange-jaune. Les cristaux atteignent une dimension maximale de 1 mm, et ont une

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allure en bloc ou prismatique selon [100]. Le minéral est transparent, et possède un éclat subadamantin; il ne montre aucune fluorescence en lumière ultraviolette (onde longue ou courte). La rakovanite est cassante, avec une dureté de Mohs de 1. Nous n'avons observé aucun clivage ou plan de séparation, et les fractures sont conchoïdales. La densité calculée à partir de la formule idéale et de la maille affinée d'un monocristal est 2.407 g cm^{-3}. La rakovanite est biaxe (+), avec α_{589nm} = 1.776(5), β_{589nm} = 1.803(5), γ_{589nm} = 1.910(6). Les valeurs mesurées de 2*V* sont: $2Vz_{540nm}$ = 58(1); $2Vz_{589nm}$ = 56(1); $2Vz_{650nm}$ = 53(1)°. La dispersion est $r < v$, intense et parallèle; orientation: $X = \mathbf{b}$; $Z \wedge \mathbf{c} = 8°$ dans l'angle obtus β. Le schéma pléochroïque est *X* jaune pâle, *Y* jaune orangé, *Z* orange jaunâtre, $Z > Y > X$. Nous avons établi la composition chimique de la rakovanite avec une microsonde électronique et par affinement de la structure. La formule empirique (V = 10 *apfu*) est $(Na_{2.90}K_{0.07}Ca_{0.01}Al_{0.01})_{\Sigma 2.99}\{H_{2.98}[V_{10}O_{28}]\}\bullet 15H_2O$, et la formule simplifiée est $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$. La rakovanite est monoclinique, groupe spatial $P2_1/n$, avec *a* 12.0248(17), *b* 17.121(3), *c* 18.140(3) Å, β 106.242(8)°, et *Z* = 4; les quatre raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(I)(*hkl*)] sont: 11.270(100)($\bar{1}$01), 7.696(81)(021), 8.709(78)(002), et 6.892(63)(120). L'agencement des atomes a été affiné jusqu'à un résidu R_1 de 0.0383; l'unité structurale est un polyanion décavanadate triplement protonné, $\{H_3[V_{10}O_{28}]\}$. Ces unités structurales sont liées par des complexes interstitiels, $(Na_3\bullet 15H_2O)$, dont le contenu neutralise la charge de +3 du polyanion décavanadate avec un groupe $NaO_4(H_2O)_2$, un dimère $Na_2(H_2O)_{10}$, et trois molécules de H_2O non liées aux cations interstitiels.

(Traduit par la Rédaction)

Mots-clés: rakovanite, nouvelle espèce minérale, décavanadate, structure cristalline, mines Sunday et West Sunday, district de Slick Rock, Colorado.

Introduction

Several new decavanadate minerals have been discovered in the West Sunday mine, Slick Rock district, San Miguel County, Colorado, USA (38° 04' 48.03" N, 108° 49' 18.07" W). One of these corresponds to the natural occurrence of $[Na_2(H_2O)_{10}][H_3V_{10}O_{28}\{Na(H_2O)_2\}]\bullet 3H_2O$, synthesized (at 25°C and pH = 4.2) and characterized by Duraisamy *et al*. (2000). We here describe the physical attributes of this mineral, which we name *rakovanite*, and the arrangement of atoms and descriptive mineralogy of that phase, recast as $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$. The name honors Dr. John Rakovan (b. 1964) of Miami University, Oxford, Ohio 45056, USA. Professor Rakovan is in the midst of a distinguished career in mineralogy, and currently serves as an Executive Editor of *Rocks and Minerals*. Professor Rakovan has served the Mineralogical Society of America in several roles, and is known for his research on the surface chemistry and structure of minerals. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2010–052). The two cotype specimens used in the description of the mineral are housed in the mineral collection of the Natural History Museum of Los Angeles County under catalogue numbers 63357 and 63358.

Background Information

Minerals of the pascoite family (pascoite: $Ca_3V_{10}O_{28}\bullet 17H_2O$) conform to the bipartite nature of mineral structures elucidated by Hawthorne (1983). Each member of the pascoite family contains the $(V_{10}O_{28})^{6-}$ decavanadate polyanion as the *structural unit*, the anhydrous anionic portion of the structure that contains bonds of higher bond-valence. In each of the minerals, the anhydrous structural units are linked by the partially or fully hydrated *interstitial complex*. The interstitial complex is the cationic portion of the structures, with bonds of lower bond-valence between alkaline and alkaline-earth cations and O atoms of the structural unit and interstitial H_2O groups (Hughes *et al*. 2008).

Although the rigid decavanadate structural units in minerals of the pascoite family are essentially identical, these minerals differ in the composition and arrangement of the interstitial complexes, whose +6 charge balances the charge of the decavanadate polyanion. Table 1 lists the known members of the pascoite family, and gives the composition of the hexavalent interstitial complex. In all cases, the charge of the decavanadate polyanion is balanced by the interstitial complex.

Synthetic decavanadate compounds are well studied (Hughes *et al*. 2005), and several such compounds are known wherein the charge of the decavanadate polyanion is balanced not only by the cationic charge of the interstitial complex but also by the protonation of oxygen atoms of the decavanadate polyanion. Duraisamy *et al*. (2000) summarized the work on these compounds, and described the atomic

TABLE 1. MEMBERS OF THE PASCOITE FAMILY

Mineral	Formula	Interstitial complex
pascoite	$Ca_3(V_{10}O_{28})\bullet 17H_2O$	$\{Ca_3(H_2O)_{17}\}^{6+}$
huemulite	$Na_4Mg(V_{10}O_{28})\bullet 23H_2O$	$\{Na_4Mg(H_2O)_{23}\}^{6+}$
hughesite	$Na_3Al(V_{10}O_{28})\bullet 22H_2O$	$\{Na_3Al(H_2O)_{22}\}^{6+}$
hummerite	$K_2Mg_2(V_{10}O_{28})\bullet 16H_2O$	$\{K_2Mg_2(H_2O)_{16}\}^{6+}$
lasalite	$Na_2Mg_2(V_{10}O_{28})\bullet 20H_2O$	$\{Na_2Mg_2(H_2O)_{20}\}^{6+}$
magnesiopascoite	$Ca_2Mg(V_{10}O_{28})\bullet 16H_2O$	$\{Ca_2Mg(H_2O)_{16}\}^{6+}$
rakovanite	$Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$	$\{Na_3(H_2O)_{15}\}^{3+}$

arrangement of one such compound, $[Na_2(H_2O)_{10}][H_3V_{10}O_{28}\{Na(H_2O)_2\}]\bullet 3H_2O$, in which the charge balance of the decavanadate polyanion is balanced by a +3 charge of the interstitial complex as well as by protonation of three oxygen atoms of the $(V_{10}O_{28})$ structural unit.

Occurrence

Rakovanite was found on specimens from the Sunday mine and the West Sunday mine, Slick Rock district, San Miguel County, Colorado, USA. The Sunday, St. Jude, and West Sunday mines are interconnected, and it is likely that the rakovanite samples that were collected are not isolated occurrences in the mining complex.

This new mineral is rare. The best crystals were found perched on an amorphous dehydrated vanadium phase along with crystals tightly adhered to a corvusite–montroseite matrix. Associated minerals include calcite, corvusite, hewettite, hughesite, montroseite, munirite, paramontroseite, pascoite, rossite, sherwoodite, and other unidentified vanadium phases, as well as at least two other potentially new decavanadate species. Uranium mineralization occurs predominantly as primary uraninite and coffinite along with minor secondary carnotite.

Rakovanite occurs as crystalline crusts on sandstone fractures in the mine walls of the Sunday and West Sunday mines. The mineral forms from the oxidation of montroseite–corvusite assemblages. Mining operations have exposed unoxidized and oxidized phases. Under ambient temperatures and generally oxidizing near-surface environments, water reacts with pyrite in the deposit to form aqueous solutions of relatively low pH. The various secondary vanadate phases that form depend upon the Eh–pH conditions and the presence of other cations (*e.g.*, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}). Mine ventilation to reduce radon levels appears to destroy many of the hydrated vanadium phases.

Appearance and Physical Properties

Crystals of rakovanite are up to 1 mm in maximum dimension and vary in habit from blocky to prismatic on [100], commonly exhibiting steps and striations parallel to [100]. Figure 1 depicts a crystal drawing of rakovanite obtained on the basis of reflecting goniometer measurements. Rakovanite is orange, with an orange-yellow streak. The mineral is transparent, with a subadamantine luster; it does not fluoresce in long- or short-wave ultraviolet radiation. Rakovanite displays brittle tenacity, and has a Mohs hardness of approximately 1. No cleavage or parting was observed, and the mineral displays a conchoidal fracture.

The density of rakovanite could not be measured because the mineral dissolves in available aqueous density-liquids, and there is insufficient material for direct measurement. The density calculated from the ideal formula and the single-crystal cell data is 2.407 g cm^{-3}, and the value calculated using the empirical formula and the single-crystal cell data is 2.409 g cm^{-3}.

Optical Properties

Spindle-stage extinction data obtained on a crystal of rakovanite provided the optical character, 2*V* and orientation of principal vibration directions (Gunter *et al*. 2004, 2005). Gladstone–Dale calculations for rakovanite predict a mean index of refraction of 1.793; however, when the crystal was placed in the 1.785 liquid, its optical orientation changed, indicating a reaction with the liquid. This reaction precluded using any of the higher-index liquids that would be required to find β or γ. Thus, to determine the higher indices of refraction, an immersion mount was made using a 1.780 liquid and a cooling–heating stage. By lowering the temperature to –8°C, a match for β was obtained, and γ was calculated on the basis of α, β, and the 2*V*z value measured at 589 nm.

Rakovanite is biaxial (+) with the following indices of refraction, measured at 589 nm: α 1.776(5), β 1.803(5), γ 1.910(6) (calculated based on α, β, and 2*V*z). The values of 2*V*z, measured at 540, 589, and 650 nm, are, respectively, 58(1), 56(1), and 53(1)°. The dispersion is $r < v$, strong, parallel; orientation: $X = \mathbf{b}$; $Z \wedge \mathbf{c} = 8°$ in obtuse β. The pleochroic scheme of rakovanite is: *X* light yellow, *Y* orangish yellow, *Z* yellowish orange, $Z > Y > X$.

The Chemical Composition of Rakovanite

Chemical analyses (10 on six crystals) were performed at the University of Utah on a Cameca SX–50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were:

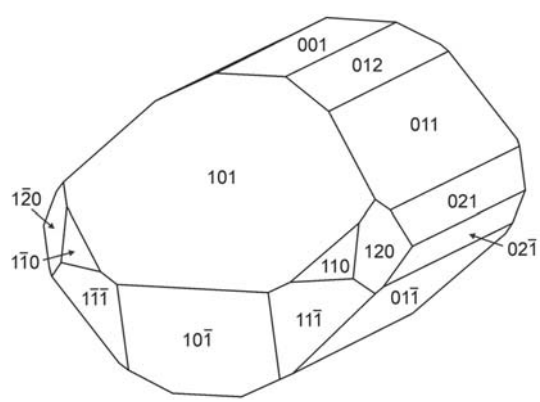

FIG. 1. Crystal drawing of rakovanite obtained on the basis of reflecting goniometer measurements.

accelerating voltage 15 keV, beam current 10 nA and a nominal beam diameter of 15 μm, although a diameter of 20 mm was occasionally used on larger fragments. Counting times were 10 seconds for each element. Where the size of the crystal permitted, the sample was slowly translated under the beam to minimize the effects of beam damage and sodium migration. Raw X-ray intensities were corrected for matrix effects with a phi-rho-z algorithm (Pouchou & Pichoir 1991). We employed as standards albite (Na), sanidine (K, Al), diopside (Mg, Ca), and V metal (V).

Preliminary analyses demonstrated that rakovanite dehydrates rapidly under the vacuum and electron beam of the microprobe. The fully hydrated composition with 15 H_2O was determined from the crystal-structure determination. The empirical formula is in excellent agreement with the results of the crystal-structure studies of the natural and synthetic materials, which yielded $Na_3(H_3V_{10}O_{28})\bullet 15H_2O$ for non-dehydrated crystals.

Table 2 presents the average result of ten analyses of six crystals of partially dehydrated rakovanite. Table 2 also presents the composition with the amount of H_2O as determined from the crystal-structure analysis and the remaining oxides normalized to [100 – (H_2O)]. The empirical formula (based on V = 10 *apfu*) is $(Na_{2.90}K_{0.07}Ca_{0.01}Al_{0.01})_{\Sigma 2.99}\{H_{2.98}[V_{10}O_{28}]\}\bullet 15H_2O$. The simplified formula of rakovanite is $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$.

Crystal Structure: Experimental

Both powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized Mo*K*α radiation. The powder data presented in Table 3 show good agreement with the pattern calculated from the structure determination.

The Rigaku CrystalClear software package was used for processing of the structure data; the structure was solved by direct methods using SIR92 (Altomare *et al*. 1994). The SHELXL–97 software (Sheldrick 2008) was used for the refinement of the structure.

The details of the data collection and structure refinement are provided in Table 4. The atomic coordinates and displacement parameters are listed in Table 5. In that table, O1–O28 are oxygen atoms of the decavanadate polyanion, and O29–O43 are oxygen atoms of the H_2O groups in the interstitial complex. Selected interatomic distances and bond valences are listed in Table 6. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Rakovanite CM49_595].

Atomic Arrangement of Rakovanite

Rakovanite, $Na_3(H_3V_{10}O_{28})\bullet 15H_2O$, is the naturally occurring analog of the phase $[Na_2(H_2O)_{10}]\ [H_3V_{10}O_{28}\{Na(H_2O)_2\}]\bullet 3H_2O$, described, including a detailed description of its structure, by Duraisamy *et al*. (2000). The structure of rakovanite, determined in this study and identical to that of the synthetic compound, consists of two distinct parts, the *structural unit* and the *interstitial complex*, as suggested by Hawthorne (1983) for such hydrated minerals with a polyanion such as the decavanadate polyanion. Below, we provide details of the structural unit and the interstitial complex in rakovanite.

The structural unit in rakovanite

The structural unit in rakovanite consists of the decavanadate polyanion, similar to that found in other decavanadate-bearing minerals (Table 1). The decavanadate polyanion is formed of ten distorted, edge-sharing octahedra. In the V1 – V8 octahedra in rakovanite, each octahedron contains one vanadyl bond, defined as a V^{5+}–O bond less than 1.74 Å in length (Schindler *et al*. 2000). In the V9 and V10 octahedra, each polyhedron has two vanadyl bonds. In all cases, the vanadyl bond is *trans* to the longest V–O bond(s) of the octahedron, which is typical of the disposition of bonds in the octahedra of the decavanadate polyanion.

The decavanadate polyanion in rakovanite differs from that found in other minerals in that it contains three hydrogen atoms, forming a $\{H_3[V_{10}O_{28}]\}^{3-}$ anionic complex. Numerous compounds with protonated decavanadate groups have been synthesized, and solids with $[V_{10}O_{28}]^{6-}$, $[HV_{10}O_{28}]^{5-}$, $[H_2V_{10}O_{28}]^{4-}$, $[H_3V_{10}O_{28}]^{3-}$, and $[H_4V_{10}O_{28}]^{2-}$ are well characterized (Duraisamy *et al*. 2000). In rakovanite, as in most protonated decavanadates (Duraisamy *et al*. 2000), the hydrogen atoms of the decavanadate polyanion are difficult to locate. Figure 2 depicts the decavanadate polyanion in rakovanite. The individual polyanions are linked by the interstitial complex, described subsequently.

Day *et al*. (1987) undertook an examination of $H_3V_{10}O_{28}[(C_6H_5)_4P]_3\bullet 4CH_3CN$ in an attempt to locate the H atoms in the triply-protonated decavanadate

TABLE 2. THE COMPOSITION OF RAKOVANITE

Oxide	wt%	Normalized wt%§	Ideal
Na_2O	8.02 (0.40)	6.90	7.15
K_2O	0.29 (0.05)	0.25	-
MgO	0.01 (0.01)	0.01	-
CaO	0.04 (0.02)	0.03	-
V_2O_5	81.2 (1.1)	69.90	69.97
Al_2O_3	0.04 (0.04)	0.03	-
H_2O*		22.87	22.87
Total		100.00	

Empirical formula (based on V = 10 *apfu*): $(Na_{2.90}K_{0.07}Ca_{0.01}Al_{0.01})_{\Sigma 2.99}\{H_{2.98}[V_{10}O_{28}]\}\bullet 15H_2O$; the ideal formula is $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$.
* H_2O calculated as ideal value for $Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$.
§ Composition normalized to 100% using ideal H_2O value from crystal-structure results.

TABLE 3. POWDER X-RAY DATA FOR RAKOVANITE

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{calc}	h	k	l
100	11.270(5)	11.1681	100	$\bar{1}$	0	1
18	9.56(2)	9.5721	10	1	1	0
		9.3540	6	$\bar{1}$	1	1
78	8.709(5)	8.7079	28	0	0	2
		8.5806	60	1	0	1
81	7.696(3)	7.6826	97	0	2	1
63	6.892(3)	6.8764	68	1	2	0
		5.8954	3	$\bar{1}$	2	2
13	5.857(8)	5.8896	3	$\bar{1}$	0	3
		5.7724	6	2	0	0
3	5.58(3)	5.5840	4	$\bar{2}$	0	2
5	4.739(9)	4.8047	2	0	2	3
		4.6869	2	1	0	3
9	4.406(6)	4.3636	3	2	2	1
		4.3539	3	0	0	4
		4.2020	2	$\bar{2}$	2	3
5	4.02(1)	4.0008	2	$\bar{3}$	0	1
		3.9914	3	$\bar{1}$	2	4
20	3.828(4)	3.8302	17	1	4	1
24	3.445(5)	3.4625	3	$\bar{1}$	4	3
		3.4382	14	2	4	0
6	3.339(6)	3.3329	3	2	2	3
		3.3278	3	$\bar{3}$	1	4
		3.2264	3	0	2	5
		3.1606	1	1	4	3
8	3.16(1)	3.1538	1	$\bar{3}$	2	4
		3.1494	3	3	1	2
14	3.034(2)	3.0302	16	2	4	2
		2.9477	16	$\bar{2}$	4	4
42	2.935(6)	2.9451	3	2	5	0
		2.9027	16	0	0	6
		2.8497	4	$\bar{1}$	2	6
		2.7939	3	3	3	2
		2.7921	1	$\bar{2}$	5	3
31	2.798(4)	2.7920	6	$\bar{4}$	0	4
		2.7701	3	1	6	0
		2.7672	2	$\bar{1}$	4	5
		2.7556	3	$\bar{4}$	1	4
		2.5901	3	1	6	2
6	2.59(2)	2.5851	1	$\bar{1}$	0	7
		2.5800	2	$\bar{4}$	1	5
12	2.524(6)	2.5360	7	4	0	2
		2.5086	4	4	1	2
24	2.433(1)	2.4261	19	$\bar{2}$	4	6
3	2.321(4)	2.3155	5	4	1	3
		2.2327	4	$\bar{2}$	5	6
14	2.194(2)	2.1957	7	$\bar{2}$	6	5
6	2.142(9)	2.1452	3	4	0	4
		2.1401	2	0	8	0
		2.1071	3	$\bar{3}$	4	7
24	2.078(1)	2.0762	7	5	1	2
		2.0748	9	$\bar{1}$	6	6
24	1.9631(7)	1.9651	13	$\bar{3}$	6	6
		1.9522	8	5	1	3
9	1.910(2)	1.9056	2	$\bar{3}$	7	5
		1.9055	6	$\bar{2}$	6	7
4	1.819(2)	1.8277	2	5	1	4
		1.8158	3	$\bar{3}$	7	6
		1.7312	3	$\bar{2}$	8	6
		1.7278	2	$\bar{6}$	5	3
11	1.724(2)	1.7273	1	$\bar{6}$	5	2
		1.7225	1	0	8	6
		1.7205	1	$\bar{3}$	7	7
		1.7189	1	$\bar{4}$	0	10
		1.7147	4	2	4	8
6	1.681(6)	1.6825	2	6	1	3
		1.6823	1	2	6	7
3	1.644(4)	1.6585	2	1	6	8
		1.6422	1	2	5	8
		1.5373	1	$\bar{4}$	9	5
12	1.5313(8)	1.5354	2	$\bar{7}$	5	3
		1.5300	1	$\bar{7}$	5	2
		1.5289	1	$\bar{7}$	5	4
3	1.487(2)	1.4896	1	$\bar{1}$	10	6
		1.4863	1	2	7	8
		1.4670	1	$\bar{4}$	1	12
4	1.462(6)	1.4616	2	3	6	8
		1.4587	2	2	6	9
1	1.454(5)	1.4552	1	$\bar{6}$	5	9
		1.4511	1	6	5	4
		1.4315	1	$\bar{4}$	10	5
		1.4278	1	$\bar{2}$	6	11
8	1.4283(5)	1.4276	1	4	1	9
		1.4268	3	0	12	0
		1.4248	1	$\bar{2}$	4	12
		1.4214	1	3	5	9
		1.4104	2	0	10	7
9	1.409(1)	1.4088	1	2	8	8
		1.4074	1	1	12	1
		1.4057	2	$\bar{7}$	7	3
		1.3892	1	$\bar{6}$	5	10
6	1.377(3)	1.3757	1	$\bar{8}$	5	3
		1.3641	1	$\bar{1}$	10	8

polyanion. The very title of their article (*Where are the protons in* $H_3V_{10}O_{28}^{3-}$*?*) illustrates the difficulty in locating the hydrogen atoms in protonated decavanadate groups. In their study, they utilized ^{17}O NMR spectroscopy to identify three oxygen atoms of the decavanadate polyanion as the likely sites for protonation in CH_3CN/H_2O solutions of $H_3V_{10}O_{28}[(n\text{–}C_4H_9)_4N]_3$. In rakovanite, bond-valence sums of the decavanadate oxygen atoms demonstrate that all decavanadate oxygen atoms would be overbonded with a hydrogen bond, suggesting that the three hydrogen atoms are disordered over those oxygen atoms. We thus conclude that, like the synthetic equivalent described by Duraisamy *et al.* (2000), the protonation sites in the decavanadate polyanion cannot be conclusively located.

The interstitial complex in rakovanite

As in other hydrated decavanadate minerals, the interstitial complex links the decavanadate structural units in rakovanite through hydrogen bonding and bonds between interstitial cations and oxygen atoms of the decavanadate polyanion (Hughes *et al.* 2008). In minerals containing non-protonated decavanate polyanions, the interstitial complexes must balance the 6– charge of that structural unit.

TABLE 4. RAKOVANITE: DATA COLLECTION AND STRUCTURE-REFINEMENT DETAILS

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation / power	Mo*K*α (λ = 0.71075 Å) / 50 kV, 40 mA
Temperature	298(2) K
Structural formula	$Na_3\{H_3[V_{10}O_{28}]\}\bullet 15H_2O$
Space group	$P2_1/n$
Unit-cell dimensions	
a, *b*	12.0248(17), 17.121(3) Å
c, β	18.140(3) Å, 106.242(8)°
Z	4
V	3585.5(9) Å^3
Density (for above formula)	2.407 g/cm^3
Absorption coefficient	2.651 mm^{-1}
F(000)	2560
Crystal size	100 × 60 × 50 μm
θ range	3.00 to 23.26°
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-20 \le l \le 20$
Reflections collected / unique	42334 / 5131 [R_{int} = 0.1096]
Reflections with $F_o > 4\sigma F$	2890
Completeness to θ = 27.48°	99.6%
Max. and min. transmission	0.8788 and 0.7774
Refinement method	Full-matrix least-squares on F^2
Parameters refined	625
GoF	0.956
Final *R* indices [$F_o > 4\sigma F$]	R_1 = 0.0383, wR_2 = 0.0739
R indices (all data)	R_1 = 0.0888, wR_2 = 0.0851
Largest diff. peak / hole	+0.437 / –0.411 *e*/Å^3

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *a* is 0.0333, *b* is 0, and *P* is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

By contrast, in rakovanite, the triply-protonated decavanadate polyanion only has a net 3– charge. In rakovanite, the ($Na_3\bullet 15H_2O$) contents balance those charges with two Na-bearing polyhedral groups and three isolated H_2O molecules. Figure 3 depicts the $NaO_4(H_2O)_2$ octahedral group, which shares O1, O2, O3 and O5 atoms with the protonated decavanadate group. Figure 4 depicts the $Na_2(H_2O)_{10}$ dimer; the interstitial group is completed by three H_2O molecules (O41, O42, O43 and associated H atoms; Table 6) that do not bond to interstitial cations. The two Na-bearing groups in the interstitial complex in rakovanite are not linked except through hydrogen bonding. The $Na_2(H_2O)_{10}$ dimer (Fig. 4) does not link directly to the decavanadate polyanion, but links through hydrogen bonding of O36–H36B...O14, O32–H32A...O27, O33–H33A...O24, O35–H35A...O13, and O34–H34A...O19. The Na1 octahedron and the Na2–Na3 dimer are linked only through hydrogen bonding of O29–H29A...O33, a contribution from the octahedron to the dimer, and O36–H36A...O29, a contribution from the dimer to the octahedron.

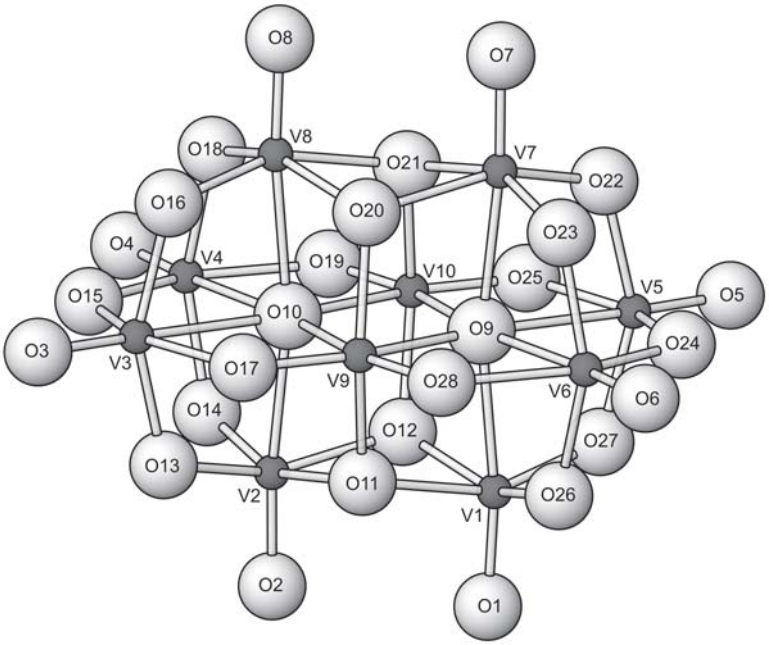

FIG. 2. The protonated decavanadate polyanion in rakovanite.

Acknowledgements

The authors gratefully acknowledge Editor-in-Chief Robert F. Martin for his long-standing contributions to mineralogy through his extraordinary service to *The Canadian Mineralogist*. The manuscript was improved by reviews by Francesco Demartin and Michael Schindler, for which we are grateful. This study was funded, in part, by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County. Jim Fisher, General Mine Superintendent, Denison Mines, allowed us to obtain specimens for study.

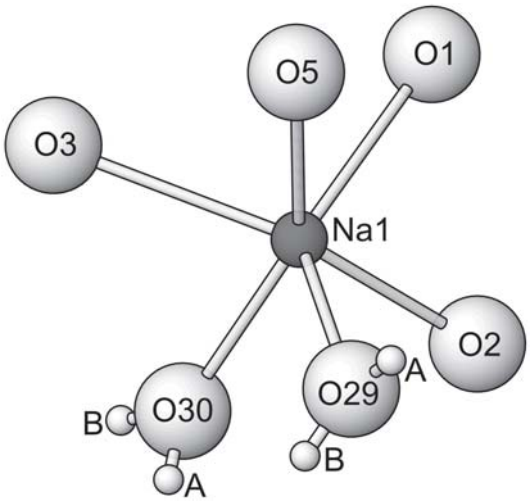

FIG. 3. The $NaO_4(H_2O)_2$ interstitial complex in rakovanite. The Na1 octahedron shares O1, O2, O3 and O5 with the decavanadate polyanion, linking the structural unit and the interstitial complex.

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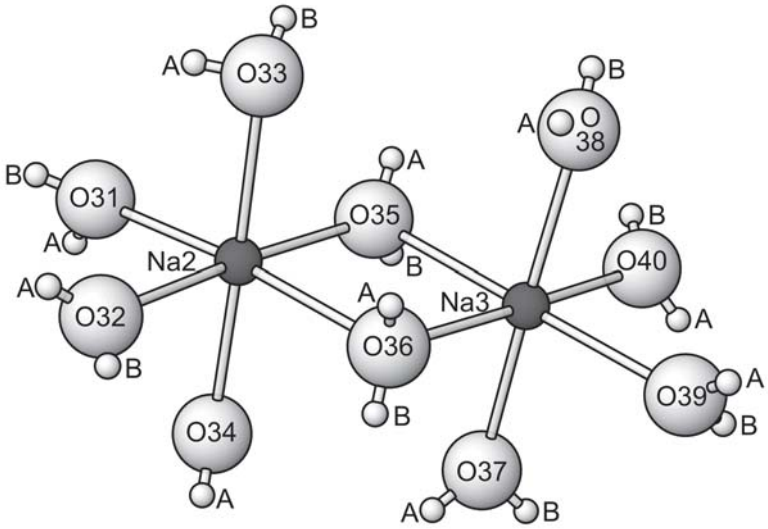

FIG. 4. The $Na_2(H_2O)_{10}$ interstitial dimer in rakovanite. The dimer, formed by the Na2 and Na3 cations and their coordinating H_2O molecules, links to the decavanadate polyanion only through hydrogen bonding.

TABLE 5. COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN RAKOVANITE

	x/a	*y/b*	*z/c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V1	0.06629(7)	-0.12903(7)	0.10294(5)	0.0195(2)	0.0198(5)	0.0252(6)	0.0118(5)	-0.0001(5)	0.0014(4)	-0.0010(5)
V2	-0.01357(7)	-0.12711(7)	0.24943(5)	0.0194(2)	0.0165(5)	0.0234(5)	0.0175(5)	0.0005(5)	0.0035(4)	-0.0011(5)
V3	0.13092(8)	-0.21570(6)	0.39482(6)	0.0212(3)	0.0249(6)	0.0206(6)	0.0184(6)	0.0031(5)	0.0065(5)	-0.0028(5)
V4	0.12453(8)	-0.03548(6)	0.39361(6)	0.0206(3)	0.0236(6)	0.0211(6)	0.0175(6)	-0.0009(5)	0.0063(5)	0.0011(5)
V5	0.28535(8)	-0.03402(6)	0.10014(6)	0.0222(3)	0.0263(6)	0.0237(6)	0.0169(6)	0.0047(5)	0.0065(5)	-0.0002(5)
V6	0.29434(9)	-0.21384(6)	0.10274(6)	0.0226(3)	0.0282(7)	0.0214(6)	0.0189(6)	-0.0026(5)	0.0079(5)	0.0011(5)
V7	0.43406(7)	-0.12108(6)	0.24686(5)	0.0182(2)	0.0187(5)	0.0206(5)	0.0151(5)	0.0001(5)	0.0047(4)	0.0005(5)
V8	0.35254(7)	-0.12222(6)	0.39303(5)	0.0181(3)	0.0187(5)	0.0199(5)	0.0144(5)	0.0004(5)	0.0029(4)	-0.0001(5)
V9	0.21232(9)	-0.22040(6)	0.24850(6)	0.0175(3)	0.0205(6)	0.0154(6)	0.0154(6)	-0.0010(5)	0.0029(4)	-0.0004(5)
V10	0.20634(8)	-0.02923(5)	0.24729(6)	0.0170(2)	0.0196(6)	0.0133(6)	0.0176(6)	0.0001(5)	0.0043(4)	0.0001(5)
Na1	0.28198(18)	0.12442(19)	-0.06503(12)	0.0394(6)	0.0355(14)	0.0560(16)	0.0272(13)	0.0038(15)	0.0095(11)	0.0021(14)
Na2	-0.19310(18)	0.13984(14)	0.16880(13)	0.0316(6)	0.0322(13)	0.0291(16)	0.0343(14)	-0.0028(12)	0.0107(11)	0.0057(11)
Na3	-0.30959(19)	0.10623(13)	0.32547(13)	0.0325(6)	0.0325(14)	0.0328(17)	0.0318(14)	-0.0036(12)	0.0083(11)	0.0038(11)
O1	-0.0685(3)	-0.1316(2)	0.05411(18)	0.0246(9)	0.020(2)	0.033(2)	0.018(2)	0.001(2)	-0.0005(16)	-0.001(2)
O2	-0.1445(3)	-0.1279(3)	0.19691(19)	0.0238(9)	0.0161(19)	0.027(2)	0.024(2)	-0.001(2)	-0.0009(22)	0.0005(19)
O3	0.1063(3)	-0.2848(2)	0.4479(2)	0.0295(11)	0.034(3)	0.026(3)	0.027(3)	0.006(2)	0.007(2)	-0.003(2)
O4	0.0949(3)	0.0321(2)	0.4462(2)	0.0271(10)	0.028(2)	0.027(3)	0.028(3)	-0.012(2)	0.011(2)	0.0034(20)
O5	0.3102(3)	0.0344(2)	0.0477(2)	0.0315(11)	0.038(3)	0.034(3)	0.024(3)	0.009(2)	0.012(2)	-0.003(2)
O6	0.3261(4)	-0.2819(2)	0.0520(2)	0.0341(11)	0.042(3)	0.034(3)	0.029(3)	-0.007(2)	0.015(2)	0.007(2)
O7	0.5663(3)	-0.1197(2)	0.29885(19)	0.0238(9)	0.016(2)	0.031(2)	0.023(2)	-0.000(2)	0.0021(16)	-0.001(2)
O8	0.4860(3)	-0.1193(2)	0.44337(19)	0.0236(9)	0.0201(20)	0.0293(23)	0.0182(20)	-0.0033(22)	0.0004(16)	-0.0022(20)
O9	0.2438(3)	-0.1249(2)	0.18500(17)	0.0160(8)	0.0197(19)	0.0160(19)	0.0110(18)	0.003(2)	0.0023(15)	0.0027(18)
O10	0.1733(3)	-0.1244(2)	0.31152(17)	0.0166(8)	0.017(2)	0.017(2)	0.016(2)	-0.0017(20)	0.0039(15)	0.0034(18)
O11	0.0566(3)	-0.1995(2)	0.1887(2)	0.0183(9)	0.020(2)	0.018(2)	0.017(2)	-0.0011(18)	0.0039(17)	-0.0040(17)
O12	0.0531(3)	-0.0549(2)	0.1874(2)	0.0174(9)	0.015(2)	0.025(2)	0.011(2)	0.0029(18)	0.0007(17)	-0.0018(17)
O13	-0.0107(3)	-0.2059(2)	0.3193(2)	0.022(10)	0.027(2)	0.021(2)	0.017(2)	0.001(2)	0.004(2)	0.004(2)
O14	-0.0162(3)	-0.0489(2)	0.3178(2)	0.0213(10)	0.017(2)	0.023(2)	0.024(2)	-0.005(2)	0.0063(18)	0.001(2)
O15	0.1005(3)	-0.1256(2)	0.44121(18)	0.0215(8)	0.023(2)	0.025(2)	0.017(2)	-0.003(2)	0.006(2)	-0.001(2)
O16	0.2911(3)	-0.2009(2)	0.4359(2)	0.0192(9)	0.025(2)	0.018(2)	0.013(2)	0.0035(18)	0.0022(18)	-0.0005(18)
O17	0.1775(3)	-0.2786(2)	0.3143(2)	0.0209(9)	0.020(2)	0.020(2)	0.021(2)	0.000(2)	0.004(2)	-0.003(2)
O18	0.2864(3)	-0.0440(2)	0.4350(2)	0.020(1)	0.018(2)	0.025(2)	0.019(2)	0.000(2)	0.007(2)	-0.003(2)
O19	0.1678(3)	0.0296(2)	0.3111(2)	0.0199(9)	0.022(2)	0.014(2)	0.023(2)	-0.001(2)	0.004(2)	-0.0008(17)
O20	0.3662(3)	-0.1947(2)	0.3095(2)	0.0177(9)	0.021(2)	0.015(2)	0.015(2)	-0.0042(18)	0.0027(17)	0.0005(17)
O21	0.3611(3)	-0.0505(2)	0.3077(2)	0.0160(9)	0.019(2)	0.015(2)	0.014(2)	-0.0044(17)	0.0031(17)	-0.0013(17)
O22	0.4274(3)	-0.0438(2)	0.1780(2)	0.0199(9)	0.017(2)	0.025(2)	0.018(2)	0.0008(18)	0.0052(17)	0.0013(18)
O23	0.4333(3)	-0.2005(2)	0.1802(2)	0.0217(9)	0.024(2)	0.019(2)	0.023(2)	-0.000(2)	0.0076(18)	0.003(2)
O24	0.3174(3)	-0.1239(3)	0.05489(18)	0.0238(9)	0.027(2)	0.029(2)	0.017(2)	-0.001(2)	0.008(2)	0.001(2)
O25	0.2403(3)	0.0302(2)	0.1819(2)	0.0178(9)	0.018(2)	0.018(2)	0.018(2)	0.001(2)	0.0055(18)	-0.0018(17)
O26	0.1321(3)	-0.2054(2)	0.0609(2)	0.0238(10)	0.027(2)	0.028(3)	0.014(2)	-0.0042(19)	0.0039(18)	-0.0022(19)
O27	0.1274(3)	-0.0487(2)	0.0606(2)	0.0212(10)	0.024(2)	0.024(2)	0.015(2)	0.0020(18)	0.0028(18)	-0.0029(18)
O28	0.2501(3)	-0.2792(2)	0.1851(2)	0.0216(10)	0.026(2)	0.018(2)	0.019(2)	-0.003(2)	0.0027(2)	-0.000(2)
O29	0.3867(4)	0.0315(3)	-0.1112(3)	0.044(1)	0.040(3)	0.042(4)	0.058(4)	0.012(3)	0.026(3)	0.002(3)
H29A	0.382(5)	-0.0128(17)	-0.097(4)	0.03(2)						
H29B	0.445(4)	0.046(4)	-0.123(4)	0.08(3)						
O30	0.3741(4)	0.2151(3)	-0.1225(3)	0.038(1)	0.036(3)	0.043(4)	0.039(3)	-0.004(3)	0.016(2)	0.002(3)
H30A	0.427(4)	0.203(4)	-0.140(4)	0.06(3)						
H30B	0.393(5)	0.2615(15)	-0.118(4)	0.04(2)						
O31	-0.1394(5)	0.2460(3)	0.0980(3)	0.040(1)	0.046(4)	0.039(3)	0.031(3)	-0.003(3)	0.004(3)	-0.014(3)
H31A	-0.078(3)	0.266(4)	0.118(4)	0.04(2)						
H31B	-0.128(5)	0.253(4)	0.057(2)	0.03(2)						
O32	-0.1075(5)	0.0522(3)	0.1008(3)	0.0414(15)	0.058(4)	0.042(4)	0.022(4)	0.004(3)	0.008(3)	0.026(3)
H32A	-0.115(4)	0.040(3)	0.0563(12)	0.008(16)						
H32B	-0.075(5)	0.025(4)	0.121(4)	0.02(2)						
O33	-0.3840(4)	0.1286(4)	0.0765(3)	0.0434(11)	0.041(3)	0.062(3)	0.030(3)	0.001(3)	0.014(2)	0.005(3)
H33A	-0.358(6)	0.141(5)	0.041(3)	0.08(3)						
H33B	-0.433(7)	0.163(5)	0.066(7)	0.17(6)						
O34	-0.0071(4)	0.1488(3)	0.2551(3)	0.0491(15)	0.037(3)	0.028(4)	0.065(4)	-0.008(3)	-0.014(3)	0.002(3)
H34A	0.047(4)	0.120(3)	0.273(3)	0.03(2)						
H34B	0.020(5)	0.191(12)	0.265(4)	0.05(3)						
O35	-0.2763(5)	0.2187(3)	0.2423(3)	0.044(2)	0.031(3)	0.049(4)	0.044(4)	-0.018(3)	-0.003(3)	0.018(3)
H35A	-0.337(3)	0.242(3)	0.224(3)	0.02(2)						
H35B	-0.243(4)	0.244(3)	0.280(2)	0.018(19)						
O36	-0.2299(5)	0.0291(3)	0.2481(3)	0.038(1)	0.037(3)	0.042(4)	0.031(3)	-0.006(3)	0.003(3)	0.007(3)
H36A	-0.278(5)	0.002(4)	0.218(3)	0.06(3)						
H36B	-0.168(4)	0.009(5)	0.270(5)	0.11(4)						

O37	-0.1203(4)	0.1231(4)	0.4046(3)	0.039(1)	0.033(3)	0.054(3)	0.029(3)	-0.003(3)	0.007(2)	0.011(3)
H37A	-0.062(3)	0.105(3)	0.396(3)	0.04(2)						
H37B	-0.101(6)	0.123(6)	0.452(1)	0.08(3)						
O38	-0.5030(5)	0.1020(3)	0.2521(3)	0.047(1)	0.049(4)	0.026(4)	0.054(4)	-0.012(3)	-0.005(3)	0.010(3)
H38A	-0.510(4)	0.065(2)	0.226(2)	-0.009(13)						
H38B	-0.560(4)	0.129(4)	0.236(4)	0.07(3)						
O39	-0.3414(5)	0.0025(3)	0.4106(3)	0.0476(14)	0.063(4)	0.046(4)	0.031(4)	-0.002(3)	0.009(3)	-0.027(3)
H39A	-0.387(4)	-0.033(2)	0.409(3)	0.024(19)						
H39B	-0.327(7)	0.019(5)	0.454(2)	0.10(4)						
O40	-0.3779(5)	0.1955(3)	0.4015(3)	0.043(1)	0.059(4)	0.043(4)	0.021(3)	-0.002(3)	0.002(3)	0.024(3)
H40A	-0.355(6)	0.186(5)	0.447(2)	0.08(3)						
H40B	-0.413(6)	0.235(3)	0.382(5)	0.09(3)						
O41	0.1760(6)	0.1302(5)	0.5923(4)	0.071(2)	0.061(4)	0.084(5)	0.079(4)	0.002(4)	0.035(3)	0.006(4)
H41A	0.213(8)	0.088(3)	0.596(6)	0.12(5)						
H41B	0.118(5)	0.126(7)	0.608(5)	0.12(4)						
O42	0.0907(4)	0.1558(3)	0.1100(3)	0.0471(14)	0.053(4)	0.040(3)	0.043(4)	0.017(3)	0.006(3)	0.012(3)
H42A	0.136(3)	0.120(2)	0.131(3)	0.008(14)						
H42B	0.088(8)	0.167(5)	0.0647(21)	0.11(4)						
O43	0.0942(5)	-0.3993(3)	0.1080(4)	0.0518(14)	0.055(4)	0.040(4)	0.055(4)	-0.002(3)	0.007(3)	0.000(3)
H43A	0.064(13)	-0.440(5)	0.087(9)	0.33(10)						
H43B	0.149(7)	-0.371(6)	0.129(6)	0.19(6)						

TABLE 6. SELECTED BOND-DISTANCES (Å) AND BOND-VALENCE VALUES (*vu*) IN RAKOVANITE

V1-			V2-			V3-			V4-		
O1	1.616(3)	1.66	O2	1.596(3)	1.75	O3	1.604(4)	1.71	O4	1.602(4)	1.72
O26	1.805(4)	0.99	O14	1.832(4)	0.92	O15	1.842(4)	0.90	O15	1.831(4)	0.93
O27	1.826(4)	0.94	O13	1.844(4)	0.90	O13	1.871(4)	0.83	O14	1.872(4)	0.83
O11	1.998(4)	0.59	O12	1.984(4)	0.61	O16	1.878(4)	0.82	O18	1.885(4)	0.80
O12	2.030(4)	0.54	O11	1.994(4)	0.60	O17	2.015(4)	0.56	O19	2.046(4)	0.52
O9	2.236(3)	0.31	O10	2.215(3)	0.33	O10	2.327(4)	0.24	O10	2.317(4)	0.25
Mean, Sum	1.919	5.03	Mean, Sum	1.911	5.11	Mean, Sum	1.923	5.00	Mean, Sum	1.926	5.05
V5-			V6-			V7-			V8-		
O5	1.590(4)	1.78	O6	1.597(5)	1.75	O7	1.606(3)	1.70	O8	1.610(3)	1.68
O24	1.835(4)	0.92	O24	1.826(4)	0.94	O22	1.807(4)	0.99	O16	1.814(4)	0.97
O27	1.850(4)	0.88	O23	1.872(4)	0.83	O23	1.818(4)	0.96	O18	1.829(4)	0.93
O22	1.895(4)	0.78	O26	1.891(4)	0.79	O21	1.997(4)	0.59	O20	2.000(4)	0.59
O25	2.038(4)	0.53	O28	2.052(4)	0.51	O20	2.016(4)	0.56	O21	2.001(4)	0.59
O9	2.339(4)	0.23	O9	2.329(4)	0.24	O9	2.250(3)	0.30	O10	2.247(3)	0.30
Mean, Sum	1.925	5.12	Mean, Sum	1.928	5.06	Mean, Sum	1.916	5.10	Mean, Sum	1.917	5.06
V9-			V10-			Na1-			Na2-		
O28	1.683(4)	1.38	O19	1.694(4)	1.34	O30	2.317(6)	0.25	O35	2.312(5)	0.25
O17	1.695(4)	1.34	O25	1.697(4)	1.33	O29	2.325(6)	0.24	O34	2.349(5)	0.23
O11	1.917(4)	0.73	O12	1.911(3)	0.75	O2	2.499(4)	0.15	O32	2.356(6)	0.22
O20	1.923(4)	0.72	O21	1.912(4)	0.74	O5	2.506(5)	0.15	O31	2.415(6)	0.19
O9	2.095(4)	0.45	O10	2.105(4)	0.44	O1	2.632(4)	0.11	O33	2.442(5)	0.18
O10	2.127(4)	0.42	O9	2.108(4)	0.44	O3	2.672(5)	0.09	O36	2.492(6)	0.15
Mean, Sum	1.907	5.04	Mean, Sum	1.905	5.04	Mean, Sum	2.492	0.99	Mean, Sum	2.394	1.22
Na3-											
O36	2.321(6)	0.24									
O38	2.335(6)	0.24									
O37	2.345(5)	0.23									
O40	2.355(5)	0.22									
O39	2.454(6)	0.17									
O35	2.546(6)	0.13									
Mean, Sum	2.393	1.23									

Bond-valence sums (*vu*) of oxygen atoms, excluding H-bonds

O1	1.77	O12	1.90	O23	1.79	O34	0.23
O2	1.90	O13	1.73	O24	1.86	O35	0.38
O3	1.80	O14	1.75	O25	1.86	O36	0.39
O4	1.72	O15	1.83	O26	1.78	O37	0.23
O5	1.93	O16	1.79	O27	1.82	O38	0.24
O6	1.75	O17	1.90	O28	1.89	O39	0.17
O7	1.70	O18	1.73	O29	0.24	O40	0.22
O8	1.68	O19	1.86	O30	0.25	O41	0
O9	1.97	O20	1.87	O31	0.19	O42	0
O10	1.98	O21	1.92	O32	0.22	O43	0
O11	1.92	O22	1.77	O33	0.18		

Constants from Brese & O'Keeffe (1991).

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Received November 26, 2010, revised manuscript accepted April 11, 2011.