

# Kyzylkumite, $\text{Ti}_2\text{V}^{3+}\text{O}_5(\text{OH})$ : new structure type, modularity and revised formula

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## ABSTRACT

The crystal structure of kyzylkumite, ideally  $\text{Ti}_2\text{V}^{3+}\text{O}_5(\text{OH})$ , from the Sludyanka complex in South Baikal, Russia was solved and refined (including the hydrogen atom position) to an agreement index,  $R_1$ , of 2.34% using X-ray diffraction data collected on a twinned crystal. Kyzylkumite crystallizes in space group  $P2_1/c$ , with  $a = 8.4787(1)$ ,  $b = 4.5624(1)$ ,  $c = 10.0330(1)$  Å,  $\beta = 93.174(1)^\circ$ ,  $V = 387.51(1)$  Å<sup>3</sup> and  $Z = 4$ . Tivanite,  $\text{TiV}^{3+}\text{O}_3\text{OH}$ , and kyzylkumite have modular structures based on hexagonal close packing of oxygen, which are made up of rutile [ $\text{TiO}_2$ ] and montroseite [ $\text{V}^{3+}\text{O}(\text{OH})$ ] slices. In tivanite the rutile:montroseite ratio is 1:1, in kyzylkumite the ratio is 2:1. The montroseite module may be replaced by the isotopic paramontroseite  $\text{V}^{4+}\text{O}_2$  module, which produces a phase with the formula  $\text{Ti}_2\text{V}^{4+}\text{O}_6$ . In the metamorphic rocks of the Sludyanka complex, vanadium can be present as  $\text{V}^{4+}$  and  $\text{V}^{3+}$  within the same mineral (e.g. in batisvite, schreyerite and berdesinskiite). Kyzylkumite has a flexible composition with respect to the  $\text{M}^{4+}/\text{M}^{3+}$  ratio. The relationship between kyzylkumite and a closely related Be-bearing kyzylkumite-like mineral with an orthorhombic norbergite-type structure from Byrud mine, Norway is discussed. Both minerals have similar X-ray powder diffraction patterns.

**KEYWORDS:** kyzylkumite, tivanite, rutile, montroseite, crystal structure, crystal chemistry, titanium, vanadium, modular structures.

## Introduction

KYZYLKUMITE was originally described with the ideal formula  $\text{V}_2^{3+}\text{Ti}_3\text{O}_9$  (Smyslova *et al.*, 1981) from the Koscheka uranium deposit in the central Kyzylkum region of Uzbekistan. Smyslova *et al.* (1981) suggested that the oxidation state of vanadium in kyzylkumite was  $\text{V}^{3+}$ , on the basis of chemical tests. The single-crystal X-ray diffraction pattern was indexed on a monoclinic unit cell with  $a = 33.80(5)$ ,  $b = 4.578(5)$ ,  $c = 19.99(3)$  Å and  $\beta = 93.40(5)^\circ$ . The X-ray powder diffraction pattern (Fig. 1*b*) was successfully indexed on this unit cell. Thus, kyzylkumite was considered to be dimorphous with schreyerite,

also ideally  $\text{V}_2^{3+}\text{Ti}_3\text{O}_9$  (Medenbach and Schmetzer, 1978; Döbelin *et al.*, 2006), although its precise crystal structure was unknown.

Anatoly Kasatkin obtained a fragment of the original kyzylkumite specimen studied by Smyslova *et al.* (1981). It consists of a single black grain embedded in epoxy. Electron-microprobe analyses yielded a total of 99.4 wt.% and a formula very close to  $\text{Ti}_4\text{V}_2\text{O}_{11}$  (A. Kasatkin, pers. comm.); such a Ti-rich composition is incompatible with a mineral that is supposed to be a dimorph of schreyerite. It was therefore decided that further research was required.

A mineral from the Byrud emerald mine, Akershus, Norway, studied by Raade and Balić-Žunić (2006), has an X-ray powder pattern (Fig. 1*a*) that is very similar to that of kyzylkumite. This mineral contains the same major elements

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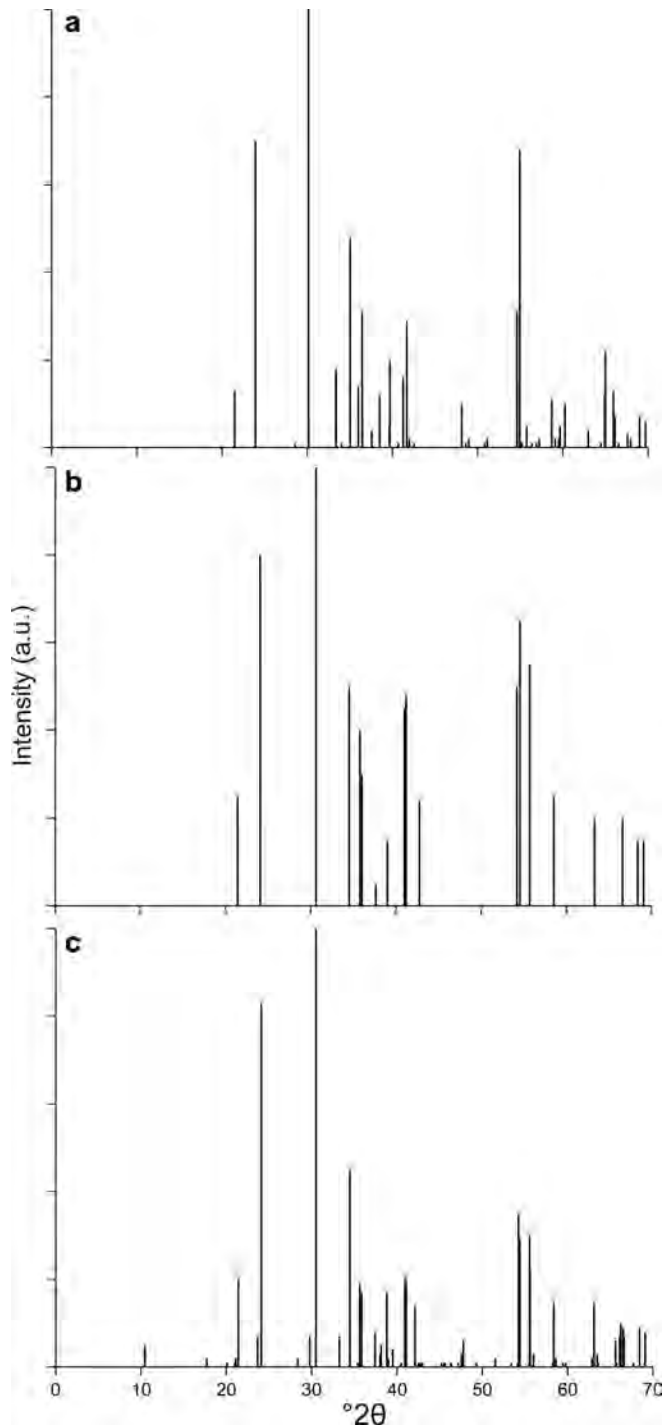


FIG. 1. X-ray powder patterns using  $\text{CuK}\alpha$  radiation (a) calculated from structural data for the kyzylkumite-like mineral  $(\text{Be}, \square)(\text{V}, \text{Ti})_3\text{O}_6$  by Raade and Balić-Žunić (2006); (b) measured by Smyslova *et al.* (1981) for kyzylkumite from the type locality; and (c) calculated from structural data for kyzylkumite from Sludyanka.

(i.e. Ti and V) as kyzylkumite, with additional minor Cr and Fe, but the analytical totals are significantly less than 100 wt.%. Single-crystal X-ray analysis on a twinned crystal suggested that the missing element was beryllium, the presence of which was subsequently confirmed by secondary ion mass spectrometry (SIMS). This is consistent with the close association with beryl. On the basis of these data, Raade and Balić-Žunić (2006) submitted a proposal to the IMA CNMNM which redefined kyzylkumite with the new formula  $(\text{Be}, \square)(\text{V}, \text{Ti})_3\text{O}_6$ . This proposal to redefine kyzylkumite was rejected by a small majority, but Raade and Balić-Žunić (2006) concluded that “a revision of kyzylkumite is necessary”. They studied a sample of kyzylkumite from the type locality (which was obtained from a mineral dealer) but not holotype or cotype material, and reported the following analysis: 0.06 wt.%  $\text{Al}_2\text{O}_3$ , 24.71 wt.%  $\text{V}_2\text{O}_3$ , 1.72 wt.%  $\text{Cr}_2\text{O}_3$ , 1.37 wt.%  $\text{Fe}_2\text{O}_3$  and 66.21 wt.%  $\text{TiO}_2$ ; total 94.07 wt.%. This analysis is significantly different to  $\text{V}_2^{3+}\text{Ti}_3\text{O}_9$ , which requires 61.52 wt.%  $\text{TiO}_2$  and 38.48 wt.%  $\text{V}_2\text{O}_3$ .

The structure of a twinned crystal of  $(\text{Be}, \square)(\text{V}, \text{Ti})_3\text{O}_6$  from the Byrud mine, Norway, was refined in space group  $Pnma$ , to produce a unit cell with  $a = 9.982(1)$ ,  $b = 8.502(1)$ ,  $c = 4.5480(6)$  Å and  $V = 385.97(9)$  Å<sup>3</sup>, which corresponds to a norbergite-like structure with Ti and V occupying octahedral and Be partially occupying tetrahedral sites.

Recently, kyzylkumite has been found in the Cr- and V-bearing metamorphic rocks of the Sludyanka complex in the South Baikal area of Russia. It has been identified based on its powder X-ray diffraction pattern (Fig. 1c) and composition which has between 62 and 70 wt.%  $\text{TiO}_2$  and between 28 and 32 wt.%  $\text{V}_2\text{O}_3$  (Reznitsky *et al.*, 2013). There is a negative correlation between Ti and (V + Cr) content, which has a slope of approximately  $-1$ . Kyzylkumite from Baikal is a late-stage secondary mineral, which replaces Ti-V oxides (schreyerite and berdesinskiite), V-bearing rutile and titanite. In previous studies it has been shown that the Ti- and V-rich minerals (batisivite, schreyerite and berdesinskiite) in the Sludyanka quartzite are characterized by isomorphous substitution of  $\text{V}^{4+}$  for  $\text{Ti}^{4+}$  (Reznitsky *et al.*, 2007, 2009; Armbruster *et al.*, 2008, 2009; Döbelin *et al.*, 2006).

The present study reports the structure and revises the ideal formula of kyzylkumite [ $\text{Ti}_2\text{V}^{3+}\text{O}_5(\text{OH})$ ]; its relationship to the Be-

bearing kyzylkumite-like mineral  $(\text{Be}, \square)(\text{V}, \text{Ti})_3\text{O}_6$  described by Raade and Balić-Žunić (2006) is also discussed.

## Experimental

Two types of dark grey opaque xenomorphic grains from the Sludyanka quartzite were studied: initial analyses of type 1 grains, which have a blue hue, by energy-dispersive spectrometry (EDS) gave a composition of *c.* 67.5 wt.%  $\text{TiO}_2$  and 31 wt.%  $\text{V}_2\text{O}_3$ ; analyses of type 2 grains, which have a red hue, gave a composition of *c.* 67 wt.%  $\text{TiO}_2$ , up to 8 wt.%  $\text{Cr}_2\text{O}_3$  and 25 wt.%  $\text{V}_2\text{O}_3$ . Single-crystal X-ray diffraction (CAD4,  $\text{MoK}\alpha$  radiation) identified the type 2 red grains as schreyerite, based on their symmetry and cell dimensions. Analyses of type 1 grains yielded unit-cell dimensions corresponding to those reported by Smyslova *et al.* (1981) for kyzylkumite. Details of the analytical procedures (electron-microprobe analyses) and variations in the composition of Sludyanka kyzylkumite [which has a mean composition corresponding to the formula  $\text{Ti}_{1.974}\text{V}_{0.937}^{3+}\text{Cr}_{0.063}\text{V}_{0.027}^{4+}\text{O}_5(\text{OH})$ ] are included in Reznitsky *et al.* (2013).

The structural data was obtained from a xenomorphic kyzylkumite single-crystal fragment from Sludyanka using a Bruker APEX II ( $\text{MoK}\alpha$  radiation) diffractometer equipped with a CCD detector (Table 1). Smyslova *et al.* (1981) were unable to find an appropriate space group, and thus the crystal was assumed to be twinned. Our research shows that the unit-cell dimensions are  $a = 8.4787(1)$ ,  $b = 4.5624(1)$ ,  $c = 10.0330(1)$  Å and  $\beta = 93.174(1)^\circ$  on the basis of  $120^\circ$  rotational twinning around **b**. The *CELL\_NOW* program (Bruker, 2011) was used to assign reflections to the different domains. Integration with two orientation matrices was performed with *SAINTE* software (Bruker, 2011). Data were corrected for absorption using *TWINABS* (Bruker, 2001). The twinning type corresponds to that reported by Raade and Balić-Žunić (2006) with the important difference that the twin individuals in the kyzylkumite-like mineral from Byrud mine, Norway, are orthorhombic, space group  $Pnma$ , with  $a = 9.982(1)$ ,  $b = 8.502(1)$ ,  $c = 4.5480(6)$  Å, whereas those in our specimen from Sludyanka are monoclinic, with  $\beta = 93.174(1)^\circ$ . An additional difference between the two diffraction patterns is the presence of simple twins in the Sludyanka sample compared to the cyclic triplets reported by Raade and Balić-Žunić (2006).

TABLE 1. Parameters for X-ray data collection and crystal-structure refinement of kyzylkumite from the Baikal Region.

|  |   |
|--|---|
| <b>Crystal data</b>                              |   |
| Unit cell dimensions                             | $a = 8.4787(1) \text{ \AA}$<br>$b = 4.5624(1) \text{ \AA}$<br>$c = 10.0330(1) \text{ \AA}$<br>$\beta = 93.174(1)^\circ$ |
| Volume   | $387.51(1) \text{ \AA}^3$   |
| Space group                                      | $P2_1/c$  |
| $Z$  | 4   |
| Ideal formula                                    | $\text{Ti}_2\text{V}^{3+}\text{O}_5(\text{OH})$   |
| <b>Intensity measurement</b>                     |   |
| Crystal shape                                    | Irregular grain   |
| Crystal size                                     | $0.05 \times 0.05 \times 0.03 \text{ mm}$   |
| Diffractometer                                   | APEX II SMART   |
| X-ray radiation                                  | $\text{MoK}\alpha$ , $\lambda = 0.71073 \text{ \AA}$  |
| X-ray power                                      | 50 kV, 30 mA  |
| Monochromator                                    | Graphite  |
| Temperature                                      | 293 K   |
| Time per frame                                   | 30 s  |
| Maximum $\theta$                                 | $30.54^\circ$   |
| Twin   | Two individuals considered  |
| Twin law   | $[-\frac{1}{2} \ 0 \ -\frac{3}{4} \   \ 0 \ -1 \ 0 \   \ -1 \ 0 \ \frac{1}{2}]$   |
| Twin contributions                               | 71.0(2)% + 29.0(2)%   |
| No. of unique reflections                        | 1150  |
| No. of observed reflections [ $I > 2\sigma(I)$ ] | 936   |
| <b>Refinement</b>                                |   |
| $R_\sigma$                                       | 0.0127  |
| $R_1$ [ $I > 2\sigma(I)$ ]                       | 0.0234  |
| $R_1$ [all data]                                 | 0.0314  |
| $wR_2$ (on $F^2$ )                               | 0.0624  |
| Goof   | 1.063   |
| $\Delta\rho_{\min}$ ( $-e \text{ \AA}^{-3}$ )    | 0.49 close to Ti1   |
| $\Delta\rho_{\max}$ ( $e \text{ \AA}^{-3}$ )     | 0.50 close to O3  |

The structure of Sludyanka kyzylkumite has been solved and refined with neutral atom scattering factors in space group  $P2_1/c$  (to  $R_1 = 2.34\%$ , for 936 reflections with  $I > 2\sigma(I)$  and 87 parameters) using the *SHELX* program package (Sheldrick, 2008). Due to the similarity of the V and Ti scattering factors, the possibility of preferred occupancy at the various octahedral sites could not be investigated. The small crystal size (Table 1) and twinning produced low diffraction intensities. Before the final refinement was made we became aware of the close structural relationship between tivanite  $\text{TiV}^{3+}\text{O}_5(\text{OH})$  (Grey and Nickel, 1981) and kyzylkumite. A hydroxylated structure was therefore considered for kyzylkumite. Analyses of bond distances between the O atoms and Ti and V revealed one O site (O5)

which had longer O–(Ti,V) bond lengths than the others. The major residual peak in the difference-Fourier map of  $\sim 0.7$  electrons was close to this position. Thus, H5 was assigned to this peak with the restraint  $d(\text{O}–\text{H}) = 0.95(1) \text{ \AA}$ . Subsequent refinements with a fixed  $U_{\text{iso}}$  of  $0.05 \text{ \AA}^2$  for the H site gave reasonable hydrogen-bond systems between oxygen donors and acceptors. To confirm hydroxylation and the presence of  $\text{Ti}^{4+}$  and  $\text{V}^{3+}$  in kyzylkumite (see discussion section) bond-valence calculations were performed using the parameters of Brown and Altermatt (1985).

## Results

Atom coordinates and displacement parameters are listed in Tables 2 and 3. Table 4 compares

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TABLE 2. Atom coordinates and isotropic-displacement parameters for kyzylkumite.

| Site | Species | $a/x$        | $b/y$       | $c/z$        | $U_{eq}$           |
|------|---------|--------------|-------------|--------------|--------------------|
| M1   | Ti      | 0.08253(4)   | -0.00466(7) | -0.12620(3)  | 0.00721(10)        |
| M2   | Ti      | 0.22693(5)   | -0.00921(7) | -0.38492(3)  | 0.00843(10)        |
| M3   | V*      | 0.39733(4)   | 0.00554(6)  | -0.65117(4)  | 0.00821(10)        |
| O1   |         | 0.07493(19)  | -0.2216(3)  | -0.29701(15) | 0.0082(3)          |
| O2   |         | 0.25205(19)  | 0.2163(3)   | -0.21405(15) | 0.0087(3)          |
| O3   |         | -0.0892(2)   | -0.2159(3)  | -0.04235(15) | 0.0089(3)          |
| O4   |         | -0.24574(19) | 0.2820(3)   | 0.05147(15)  | 0.0086(3)          |
| O5   |         | -0.41865(19) | -0.2119(3)  | 0.45759(15)  | 0.0082(3)          |
| O6   |         | 0.4144(2)    | -0.2463(3)  | -0.80111(16) | 0.0092(3)          |
| H5   |         | -0.421(4)    | -0.420(2)   | 0.452(3)     | 0.050 <sup>†</sup> |

\* The V is assigned to the M3 site based on crystal chemical criteria.

<sup>†</sup> The value listed for H5 is a fixed  $U_{iso}$  as described in the text.

In the structure refinement identical Ti scattering factors were used for all the metal sites.

interatomic distances and bond valences. The hydrogen bonds are summarized in Table 5. A crystallographic information file (cif) has been deposited with *Mineralogical Magazine*, and can be downloaded from [http://www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html). A cif for the crystal structure of kyzylkumite has also been deposited with the ICSD database of the Fachinformationszentrum at Karlsruhe, Germany.

## Discussion

The structures of kyzylkumite  $Ti_2V^{3+}O_5(OH)$  (this paper) and tivanite  $TiV^{3+}O_3(OH)$  (Grey and Nickel, 1981) are closely related. Both minerals are oxyhydroxides of Ti and  $V^{3+}$  and both

structures are based on hexagonal close packing of oxygen parallel to (010). In tivanite the Ti:V ratio is one; in kyzylkumite the Ti:V ratio is two. In tivanite, chains of edge-sharing  $MO_6$  octahedra run parallel to [102]. These chains are displaced by a  $V^{3+}O_6$  dimer after two Ti octahedra (Fig. 2). The corresponding topology is shown for kyzylkumite (Fig. 3) with chains running parallel to  $[10\bar{1}]$  but the displacement by the dimers occurs after four octahedra (M2–M1–M1–M2).

### Modularity and chemical flexibility

A modular relationship becomes apparent if larger (010) sections of the tivanite and kyzylkumite structure are drawn (Fig. 4). Grey and Nickel

TABLE 3. Anisotropic-displacement parameters for the metal sites in kyzylkumite.

| Site | Species | $U_{11}$    | $U_{22}$    | $U_{33}$    | $U_{23}$     | $U_{13}$    | $U_{12}$     |
|------|---------|-------------|-------------|-------------|--------------|-------------|--------------|
| M1   | Ti      | 0.00681(19) | 0.00821(16) | 0.00667(18) | -0.00016(10) | 0.00079(13) | -0.00003(11) |
| M2   | Ti      | 0.00867(19) | 0.00946(17) | 0.00726(17) | 0.00006(11)  | 0.00144(12) | 0.00050(12)  |
| M3   | V*      | 0.00677(18) | 0.00808(15) | 0.00986(17) | 0.00082(11)  | 0.00128(12) | 0.00139(12)  |
| O1   | O       | 0.0087(8)   | 0.0090(5)   | 0.0072(7)   | -0.0006(4)   | 0.0017(5)   | -0.0024(5)   |
| O2   | O       | 0.0075(8)   | 0.0095(5)   | 0.0091(7)   | 0.0002(5)    | -0.0002(6)  | -0.0016(5)   |
| O3   | O       | 0.0088(8)   | 0.0095(5)   | 0.0082(7)   | -0.0001(4)   | 0.0007(5)   | -0.0024(5)   |
| O4   | O       | 0.0080(8)   | 0.0097(5)   | 0.0082(7)   | 0.0015(4)    | 0.0003(6)   | 0.0024(5)    |
| O5   | O       | 0.0077(7)   | 0.0080(5)   | 0.0088(7)   | 0.0003(4)    | 0.0009(5)   | -0.0009(5)   |
| O6   | O       | 0.0066(8)   | 0.0104(5)   | 0.0106(7)   | -0.0022(4)   | 0.0011(6)   | -0.0006(4)   |

\* The V has been assigned based on crystal chemical criteria.

In the structure refinement Ti scattering factors were used for all metal sites.

TABLE 4. Bond lengths (Å) and bond-valence values and sums (vu) for kyzylkumite.

| Bond    | Bond length   | BV   | BV sum | * $\Delta$ |
|---------|---------------|------|--------|------------|
| Ti1–O3  | 1.9659(15)    | 0.67 |        |            |
| Ti1–O3  | 1.9727(16)    | 0.65 |        |            |
| Ti1–O1  | 1.9770(14)    | 0.65 |        |            |
| Ti1–O1  | 1.9824(14)    | 0.64 |        |            |
| Ti1–O4  | 1.9908(14)    | 0.62 |        |            |
| Ti1–O2  | 1.9997(16)    | 0.61 |        |            |
| <Ti1–O> | <b>1.9814</b> |      | 3.84   | 0.0338     |
| Ti2–O1  | 1.8718(16)    | 0.87 |        |            |
| Ti2–O3  | 1.8956(15)    | 0.8  |        |            |
| Ti2–O4  | 1.9376(15)    | 0.72 |        |            |
| Ti2–O2  | 2.0006(14)    | 0.61 |        |            |
| Ti2–O5  | 2.0791(16)    | 0.49 |        |            |
| Ti2–O6  | 2.0812(16)    | 0.49 |        |            |
| <Ti2–O> | <b>1.9778</b> |      | 3.97   | 0.2094     |
| V3–O2   | 1.8548(14)    | 0.74 |        |            |
| V3–O6   | 1.9047(15)    | 0.65 |        |            |
| V3–O4   | 1.9583(15)    | 0.56 |        |            |
| V3–O6   | 2.0355(16)    | 0.45 |        |            |
| V3–O5   | 2.1025(15)    | 0.38 |        |            |
| V3–O5   | 2.1568(15)    | 0.33 |        |            |
| <V3–O>  | <b>2.0021</b> |      | 3.11   | 0.3020     |
| O1–Ti1  | 1.9824(14)    | 0.64 |        |            |
| O1–Ti1  | 1.9770(14)    | 0.65 |        |            |
| O1–Ti2  | 1.8718(16)    | 0.86 |        |            |
|         |               |      | 2.15   |            |
| O2–V3   | 1.8548(14)    | 0.74 |        |            |
| O2–Ti1  | 1.9997(16)    | 0.61 |        |            |
| O2–Ti2  | 2.0006(14)    | 0.61 |        |            |
|         |               |      | 1.96   |            |
| O3–Ti2  | 1.8956(15)    | 0.8  |        |            |
| O3–Ti1  | 1.9659(15)    | 0.67 |        |            |
| O3–Ti1  | 1.9727(16)    | 0.65 |        |            |
|         |               |      | 2.12   |            |
| O4–Ti2  | 1.9376(15)    | 0.72 |        |            |
| O4–V3   | 1.9583(15)    | 0.74 |        |            |
| O4–Ti1  | 1.9908(14)    | 0.62 |        |            |
| O4–H5   | 3.106(2)      | 0.07 |        |            |
|         |               |      | 2.15   |            |
| O5–Ti2  | 2.0791(16)    | 0.49 |        |            |
| O5–V3   | 2.1025(15)    | 0.38 |        |            |
| O5–V3   | 2.1568(15)    | 0.33 |        |            |
| O5–H5   | 0.951(10)     | 0.8  |        |            |
| O5–H5   | 3.110(3)      | 0.07 |        |            |
|         |               |      | 2.07   |            |
| O6–V3   | 2.0355(16)    | 0.45 |        |            |
| O6–V3   | 1.9047(15)    | 0.74 |        |            |
| O6–Ti2  | 2.0812(16)    | 0.49 |        |            |
| O6–H5   | 2.901(2)      | 0.07 |        |            |
|         |               |      | 1.75   |            |

\* The parameter  $\Delta = (\text{Ti}-\text{O})_{\text{max}} - (\text{Ti}-\text{O})_{\text{min}}$ .

Bond-valence values are calculated using the parameters of Brown and Altermatt (1985).

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TABLE 5. Hydrogen bonds in kyzylkumite.

| D–H (Å)   | H···A (Å) | D···A (Å) | <(DHA) (°) | D–H···A    |
|-----------|-----------|-----------|------------|------------|
| 0.951(10) | 2.12(2)   | 2.901(2)  | 138(3)     | O5–H5···O6 |
| 0.951(10) | 2.37(3)   | 3.110(3)  | 134(3)     | O5–H5···O5 |
| 0.951(10) | 2.40(3)   | 3.106(2)  | 130(3)     | O5–H5···O4 |

D = donor oxygen, A = acceptor oxygen.

(1981) noticed that the tivanite structure can be derived from a rutile-type structure by the application of the antiphase operation  $\frac{1}{2}[013](0\bar{3}1)$  (shear vector followed by shear plane), which produces slices of diaspore structure type. Thus tivanite,  $\text{TiV}^{3+}\text{O}_3(\text{OH})$ , can be described as a modular structure which is

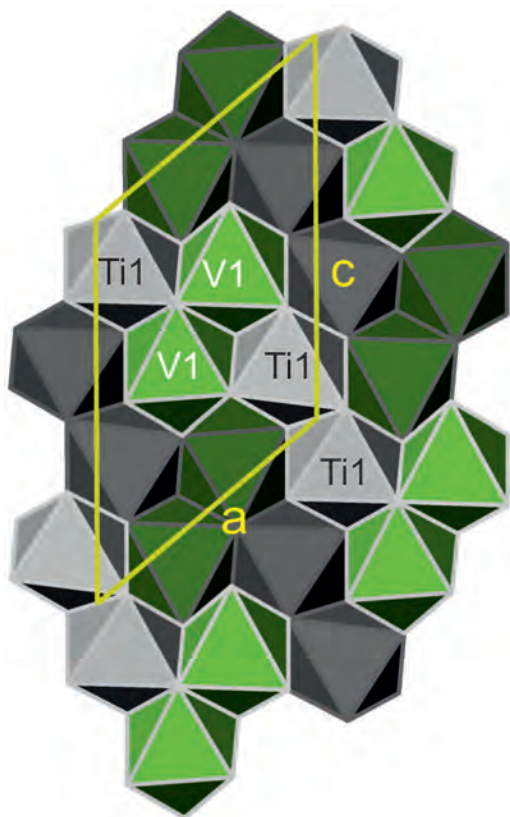


FIG. 2. Crystal structure of tivanite (Grey and Nickel, 1981) projected along **b**: octahedra with white rims form the upper layer, those with grey rims the lower layer; unit-cell outlines are shown in yellow.

composed of alternating  $\text{TiO}_2$  (rutile) and montroseite ( $\text{V}^{3+}, \text{Fe}^{2+}, \text{V}^{4+}$ ) $\text{O}(\text{OH})$  (Evans and Block, 1953) blocks in a 1:1 ratio (Fig. 4). The structure of kyzylkumite can be derived from the rutile-structure type by the same type of antiphase operations to produce an alternating sequence composed of two rutile-type slices and a single montroseite-type slice (Fig. 4). This structure allows pronounced flexibility in chemical composition, in particular regarding the ratio of four- and three-valent cations. The cause is the strong structural relationship between montroseite ( $\text{V}^{3+}, \text{Fe}^{2+}, \text{V}^{4+}$ ) $\text{O}(\text{OH})$  and paramontroseite  $\text{VO}_2$  (Evans and Mrose, 1955). Both structures have the same symmetry and topology of the diaspore-structure type with the important difference that paramontroseite has no (OH) and only contains  $\text{M}^{4+}$ . Thus depending on the degree of hydroxylation, the  $\text{M}^{4+}/\text{M}^{3+}$  ratio of kyzylkumite may exceed the value of 2 in the endmember formula. Furthermore, stacking faults in the sequence of modules, such as the intercalation of tivanite units or even extended rutile-type blocks, extend the structural possibilities.

The degree of hydroxylation of kyzylkumite from the Sludyanka complex is difficult to establish. The X-ray scattering power of H is low and does not allow a reliable site-occupancy refinement. Neutron diffraction techniques cannot be used due to the small crystal size and limited availability of homogeneous material. Nevertheless, one OH group was located in the structure refinement, leading to an ideal formula  $\text{Ti}_2\text{V}^{3+}\text{O}_5(\text{OH})$ . We may speculate from the peak height in the difference-Fourier map that occupancy of the H5 site is at least 75%. The  $\text{M}^{4+}/\text{M}^{3+}$  ratio cannot be evaluated simply; in quartzites of the Sludyanka complex, schreyerite (Döbelin *et al.*, 2006), batisivite (Reznitsky *et al.*, 2007; Armbruster *et al.*, 2008) and berdesinskiite (Reznitsky *et al.*, 2009; Armbruster *et al.*, 2009) contain variable amounts of  $\text{V}^{4+}$  and  $\text{V}^{3+}$ . The



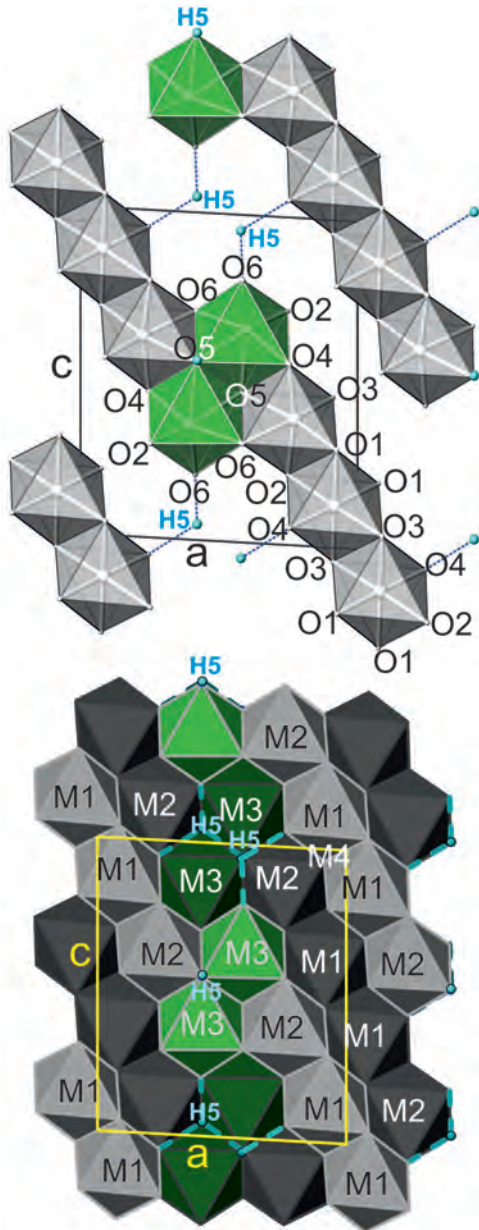


FIG. 3. Crystal structure of kyzylkumite (this study), projected along **b**: green octahedra (M3) represent  $V^{3+}$  sites and grey octahedra (M1 and M2) are enriched in Ti. Only one (010) layer is shown in the upper figure with transparent octahedra allowing insight into polyhedral distortions; hydrogen bonds are indicated by dashed blue lines. Two (010) layers are shown in the lower figure. Octahedra in the upper layer have white rims, those in the lower layer have grey rims, unit-cell outlines are shown in yellow.

flexibility of the kyzylkumite structure may also explain why strongly diverging  $Ti^{4+}/(V^{3+} + Cr^{3+})$  ratios were reported by Raade and Balić-Žunić (2006) and Smyslova *et al.* (1981) for kyzylkumite from the Koscheka uranium deposit in central Kyzylkum, Uzbekistan.

Grey *et al.* (1983) used hydrothermal experiments to show that nanocrystalline pseudorutile forms single-phase products within the compositional range  $0.2 \leq Ti/(Ti + Fe) \leq 0.6$ . The structures of these nanomaterials may be explained by modular combinations of the rutile ( $TiO_2$ ) and the goethite ( $FeOOH$ ) structures expressed by the formula  $(FeOOH)_{2p}(TiO_2)_q$  in which  $p$  and  $q$  are integers. The extreme compositions for synthetic pseudorutile were  $Fe_2Ti_3O_8(OH)_2$  (with  $p = 1, q = 3$ ) and  $Fe_4TiO_6(OH)_4$  (with  $p = 2, q = 1$ ). A similar notation system for compounds in the system  $V_2O_3-TiO_2-H_2O$  would yield  $(VOOH)_{2p}(TiO_2)_q$ ; with tivanite,  $Ti_2V_2^{3+}O_6(OH)_2$ , corresponding to  $p = 1, q = 2$  and Sludyanka kyzylkumite,  $Ti_4V_3^{3+}O_{10}(OH)_2$ , corresponding to  $p = 1, q = 4$ .

#### Order of $Ti^{4+}$ and $V^{3+}$

Although the difference in scattering power does not allow V and Ti to be distinguished at the octahedral sites, there are four strong crystal-chemical arguments for an ordered Ti, V distribution in kyzylkumite. (1) To avoid ‘over-bonding’, the O5 oxygen site, which acts as donor of a hydrogen bond, should be preferentially bonded to  $V^{3+}$ . All oxygen sites in kyzylkumite are coordinated by three M sites. Inspection of Table 4 indicates that O5 is bonded to  $2 \times M3$  and  $1 \times M2$ . Thus  $V^{3+}$  is assumed to be located at M3. (2) The M3 atom has a mean M–O bond length of  $\sim 2.00$  Å, whereas M1 and M2 have mean M–O distances of  $\sim 1.98$  Å (Table 4). The longer mean bond length for octahedral  $V^{3+}$  compared to  $Ti^{4+}$  is in accord with the corresponding ionic radii of 0.64 Å and 0.605 Å, respectively (Shannon, 1976). (3) The assignment corresponds approximately to the analysed Ti/(V + Cr) ratio (for variations in the composition see discussion above). (4) The assumption that M3 contains  $V^{3+}$  agrees with the corresponding assignment in the topologically related structure of tivanite (Grey and Nickel, 1981).

#### Hydrogen bonds

The hydrogen site in kyzylkumite has trifurcated hydrogen bonds (Fig. 5) to the adjacent close-



KYZYLKUMITE, A NEW STRUCTURE TYPE

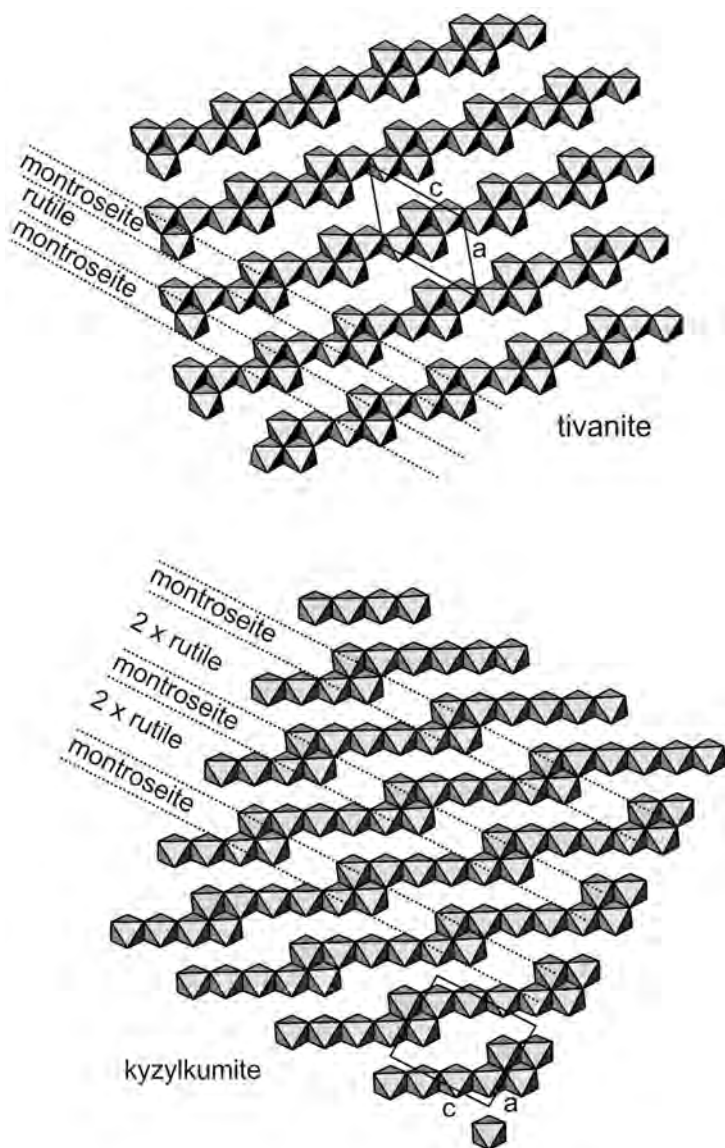


FIG. 4. Interpretation of the structure of tivanite and kyzylkumite as derivatives of the rutile-structure type (Grey and Nickel, 1981). Repeated antiphase operations  $\frac{1}{2}[013](0\bar{3}1)$  (referring to the rutile structure-type) indicated by dashed lines lead to intercalated modular slices of the diaspore-structure type, which is described as montroseite [i.e.  $V^{3+}O(OH)$ ] herein. In tivanite the rutile:montroseite ratio is 1:1; it is 2:1 in kyzylkumite.

packed oxygen layers (Table 5). With O—H...O distances between 2.9 and 3.1 Å the hydrogen bonds are rather weak. In bond-valence calculations (Table 4) we have assigned 0.8 valence units (vu) to the donor oxygen and 0.07 vu to each of the three acceptor oxygen atoms (Ferraris and Ivaldi, 1988).

*Revised density*

In addition to the unit cell and symmetry of kyzylkumite, there are two important revisions to the description of Smyslova *et al.* (1981). (1) Kyzylkumite from the Sludyanka complex is not dimorphous with schreyerite (ideally  $V_2Ti_3O_9$ ). If

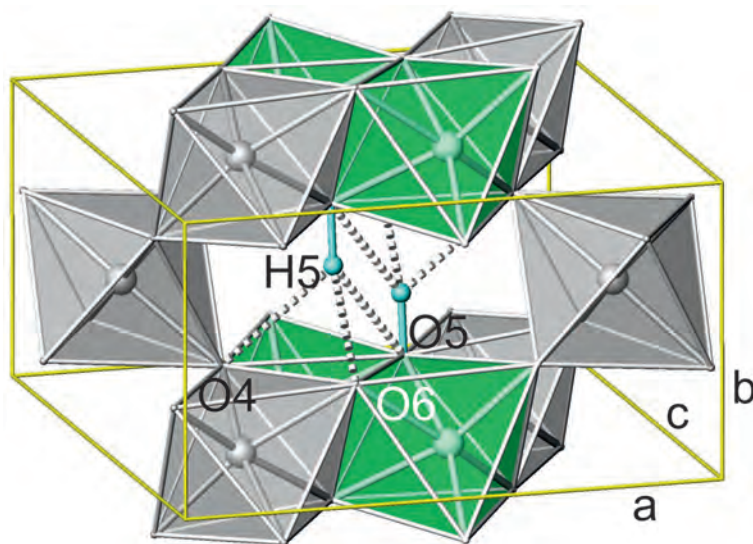


FIG. 5. Hydrogen bonding in kyzylkumite: in the diaspore-like channels of the montroseite module, H5 has trifurcated hydrogen bonds to O4, O5 and O6. The  $V^{3+}$  octahedra are green and the  $Ti^{4+}$  octahedra are grey.

it is written with the same V:Ti ratio as schreyerite, the formula of kyzylkumite becomes  $Ti_{1.8}V_{1.0}^{3+}V_{0.2}^{4+}O_5(OH)$  or  $Ti_{1.8}V_{1.2}^{4+}O_6$  depending on whether the montroseite or paramontroseite module is included in the structure. (2) The density of  $3.75\text{--}3.77\text{ g cm}^{-3}$  reported by Smyslova *et al.* (1981) for kyzylkumite is too low. Our crystal structure data and the ‘ideal’ composition,  $Ti_2V^{3+}O_5(OH)$ , produce a calculated density of  $4.15\text{ g cm}^{-3}$ . The higher density compared to the value reported by Smyslova *et al.* (1981) is corroborated by comparison with structurally and chemically related minerals. Montroseite, paramontroseite and tivanite have calculated densities between  $4.1$  and  $4.2\text{ g cm}^{-3}$ , and berdesinskiite and schreyerite have densities of  $\sim 4.5\text{ g cm}^{-3}$ . The Be-bearing kyzylkumite-like mineral described by Raade and Balić-Žunić (2006) has a calculated density of  $4.3\text{ g cm}^{-3}$ .

#### *Structural relation between kyzylkumite and the Be-bearing kyzylkumite-like mineral*

The occurrence of a Be-bearing kyzylkumite-like mineral similar to that described by Raade and Balić-Žunić (2006) in the metamorphic quartzites of the Sludyanka complex is very unlikely as there is no known pegmatite body which contain Be mineralization. However, the similarities in the

X-ray powder patterns (Fig. 1), twin diffraction patterns, and transition-element chemistry are striking and invite discussion. Kyzylkumite (this study) and the norbergite-type structure of the Be-bearing kyzylkumite-like mineral (Raade and Balić-Žunić, 2006) are both based on hexagonal close packing of oxygen, which produces a  $4.5\text{ \AA}$  periodicity parallel to the stacking direction. The light Be ion has a low X-ray scattering power and a negligible influence on the powder X-ray diffraction pattern compared to the transition-metal ions (M). Both structures have the same O:M ratio of 2:1, indicating that 50% of the octahedral voids are occupied. In the structure of the Be-bearing mineral from Norway (Raade and Balić-Žunić, 2006), M-bearing octahedra occur in continuous zigzag chains running parallel to **b** (Fig. 6) whereas the kyzylkumite structure is characterized by staggered chain fragments, each six octahedra long (Fig. 4). By omission of the Be tetrahedra combined with a shift of one octahedron per unit cell to a different position, the structure of the kyzylkumite-like mineral (Raade and Balić-Žunić, 2006) can be modified to produce kyzylkumite (Fig. 6). Thus, the Be vacancies in the norbergite-type structure described by Raade and Balić-Žunić (2006) may possibly be explained by coherent intergrowth with kyzylkumite.

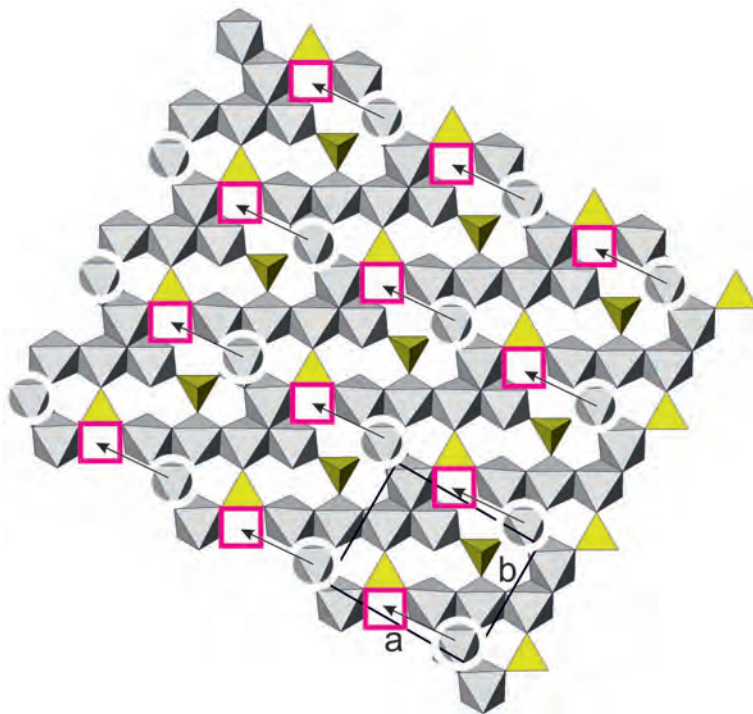


FIG. 6. Structural relationship between the Be-bearing kyzylkumite-like mineral with the norbergite-type structure (Raade and Balić-Žunić, 2006) and kyzylkumite (this study). Omitting the yellow Be tetrahedra in the structure of the kyzylkumite-like mineral and shifting (arrow) the octahedra marked by white circles to the red squares yields the topology of the kyzylkumite structure determined in this paper. In a comparison with Fig. 4 (kyzylkumite) the staggered arrangement of the chain fragments of six octahedra becomes apparent after the modification.

Zhang *et al.* (2005) reported an unnamed mineral of the ‘kyzylkumite group’, with a formula  $\text{Fe}_2^{3+}\text{Sn}_3\text{O}_9$ , in association with cassiterite, scheelite, beryl and apatite, from a W-Sn deposit in Pingwu, China. The assignment to the ‘kyzylkumite group’ was justified by the monoclinic unit-cell dimensions,  $a = 33.75$ ,  $b = 4.57$ ,  $c = 20.01$  Å and  $\beta = 93^\circ 24'$ , and the stoichiometry, which is similar to that reported by Smyslova *et al.* (1981) for kyzylkumite. However, the X-ray powder pattern reported by Zhang *et al.* (2005) is not similar to the calculated pattern for kyzylkumite from Sludyanka (this paper) even if the scattering factors for Ti are replaced by those for Sn. In view of the description of  $(\text{Be}, \square)(\text{V}, \text{Ti})_3\text{O}_6$ , with a norbergite-like structure by Raade and Balić-Žunić (2006), it is worthwhile emphasizing that the supposed ‘kyzylkumite-group’ mineral  $\text{Fe}_2^{3+}\text{Sn}_3\text{O}_9$  was found in beryl-bearing rocks. Its structural relationship to other minerals remains unresolved.

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O2 O 0.25205(19) 0.2163(3) -0.21405(15) 0.0087(3) Uani 1 1 d . . .
O3 O -0.0892(2) -0.2159(3) -0.04235(15) 0.0089(3) Uani 1 1 d . . .
O4 O -0.24574(19) 0.2820(3) 0.05147(15) 0.0086(3) Uani 1 1 d . . .
O5 O -0.41865(19) -0.2119(3) 0.45759(15) 0.0082(3) Uani 1 1 d D . .
O6 O 0.4144(2) -0.2463(3) -0.80111(16) 0.0092(3) Uani 1 1 d . . .
H5 H -0.421(4) -0.420(2) 0.452(3) 0.050 Uiso 1 1 d D . .

```

```

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  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
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M2 0.00867(19) 0.00946(17) 0.00726(17) 0.00006(11) 0.00144(12) 0.00050(12)
M3 0.00677(18) 0.00808(15) 0.00986(17) 0.00082(11) 0.00128(12) 0.00139(12)
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O2 0.0075(8) 0.0095(5) 0.0091(7) 0.0002(5) -0.0002(6) -0.0016(5)
O3 0.0088(8) 0.0095(5) 0.0082(7) -0.0001(4) 0.0007(5) -0.0024(5)
O4 0.0080(8) 0.0097(5) 0.0082(7) 0.0015(4) 0.0003(6) 0.0024(5)
O5 0.0077(7) 0.0080(5) 0.0088(7) 0.0003(4) 0.0009(5) -0.0009(5)
O6 0.0066(8) 0.0104(5) 0.0106(7) -0.0022(4) 0.0011(6) -0.0006(4)

```

```

#-----#
#                               MOLECULAR GEOMETRY                               #
#-----#

```

```

_geom_special_details

```

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;
All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell s.u.'s are taken
into account individually in the estimation of s.u.'s in distances, angles
and torsion angles; correlations between s.u.'s in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
;

```

```

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M1 O4 1.9908(14) 3 ?  
M1 O2 1.9997(16) . ?  
M1 M2 2.9307(4) . ?  
M1 M1 2.9607(6) 3 ?  
M2 O1 1.8718(16) . ?  
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M2 O2 2.0006(14) . ?  
M2 O5 2.0791(16) 3 ?  
M2 O6 2.0812(16) 4\_556 ?  
M2 M3 3.1072(5) . ?  
M2 M3 3.1864(5) 3\_654 ?  
M3 O2 1.8548(14) 4\_565 ?  
M3 O6 1.9047(15) . ?  
M3 O4 1.9583(15) 2\_544 ?  
M3 O6 2.0355(16) 2\_653 ?  
M3 O5 2.1025(15) 1\_654 ?  
M3 O5 2.1568(15) 3 ?  
M3 M2 3.1864(5) 3\_654 ?  
O1 M1 1.9824(14) 2\_544 ?  
O2 M3 1.8548(14) 4\_566 ?  
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