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This study presents the first structural report of kolbeckite, with the ideal formula ScPO$_4$$^\cdot$2H$_2$O (scandium phosphate dihydrate), based on single-crystal X-ray diffraction data. Kolbeckite belongs to the metavariscite mineral group, in which each PO$_4$ tetrahedron shares four vertices with four ScO$_4$(H$_2$O)$_2$ octahedra and vice versa, forming a three-dimensional network of polyhedra.

Comment

A number of phosphates and arsenates belong to the orthorhombic (Pbc,$a$/n) variscite and monoclinic (P2$_1$/n) metavariscite mineral groups with a general chemical formula AXO$_4$-2H$_2$O, where A = Al$^{3+}$, Fe$^{3+}$, Sc$^{3+}$, In$^{3+}$ or Ga$^{3+}$, and X = P$^{5+}$ or As$^{5+}$. The crystal chemistry of these compounds has been investigated extensively because of the biological and geochemical importance of phosphorus and arsenic, especially their roles in soils, water, and waste management (e.g. Huang & Shenker, 2004; O’Day, 2006). Recent studies have also revealed that variscite- and metavariscite-type materials possess interesting microporous and absorption properties (Tang et al., 2002, and references therein). To date, structural determinations have been conducted for the following variscite- and metavariscite-type materials: Pbc,$a$ and P2$_1$/n Al(PO$_4$)$_2$-2H$_2$O (Kniep & Mootz, 1973; Kniep et al., 1977), Pbc,$a$ and P2$_1$/n Fe(PO$_4$)$_2$-2H$_2$O (Moore, 1966; Song et al., 2002; Taxer & Bartl, 2004), P2$_1$/n In(PO$_4$)$_2$-2H$_2$O (Sugiyama et al., 1999; Tang et al., 2002), Pbc,$a$ Al(AsO$_4$)$_2$-2H$_2$O (Harrison, 2000), Fe(AsO$_4$)$_2$-2H$_2$O (Hawthorne, 1976), In(AsO$_4$)$_2$-2H$_2$O (Tang et al., 2002), and Ga(PO$_4$)$_2$-2H$_2$O (Loiseau et al., 1998). The structural relationships between the two groups of compounds have been discussed by Moore (1966), Loiseau et al. (1998), and Taxer & Bartl (2004). Kolbeckite, which was also previously called eggonite or sterrettite, is a scandium phosphate mineral with the ideal chemical formula Sc(PO$_4$)$_2$-2H$_2$O and a monoclinic unit cell comparable with that of metavariscite [see the review by Hey et al. (1982)]. However, in spite of the long time since its first description (Schräuf, 1879), the crystal structure of kolbeckite remained undetermined. This study presents the first structure refinement of kolbeckite based on single-crystal X-ray diffraction data.

The structure of kolbeckite, which is homologous with metavariscite, consists of two basic polyhedral units, viz. PO$_4$ tetrahedra and ScO$_4$(H$_2$O)$_2$ octahedra. Each PO$_4$ tetrahedron shares four vertices with four ScO$_4$(H$_2$O)$_2$ octahedra and vice versa, forming a three-dimensional network of polyhedra (Fig. 1). The two H$_2$O molecules (O5 and O6) coordinated to Sc$^{3+}$ are in cis positions, and the Sc–O5 and Sc–O6 distances are noticeably longer than the other four Sc–O bond lengths. The average interatomic P–O (1.527 Å) and Sc–O (2.080 Å) distances in kolbeckite are in agreement with those reported in the literature. Nevertheless, the bond-valence-sum calculations (Brown, 1996) indicate that P$^{5+}$ is slightly under-bonded (4.926 valence units, v.u.), whereas Sc$^{3+}$ is over-bonded (3.24 v.u.). The U$_{33}$ parameter of atom O5 in kolbeckite is significantly larger than the U$_{11}$ or U$_{22}$ parameters. A similar observation has been reported for other metavariscite-type materials, such as Al(PO$_4$)$_2$-2H$_2$O (Kniep & Mootz, 1973), In(PO$_4$)$_2$-2H$_2$O (Sugiyama et al., 1999) and Fe(PO$_4$)$_2$-2H$_2$O (Song et al., 2002), thus suggesting a possible disordered distribution of this water molecule in the channels along the c axis.

As observed in other metavariscite-type compounds, the Sc1–O5 and Sc1–O6 bond distances of 2.116 (4) and 2.178 (4) Å, respectively, are significantly different, indicating distinct bonding environments for the two H$_2$O molecules. In fact, the hydrogen bonds involving atoms H1A and H1B are both shorter than those involving atoms H2A and H2B.
Experimental

The kolkbeckite specimen used in this study is from Hot Springs County, Arkansas, USA, and is in the collection of the RRUFF project (deposition no. R060981; http://rruff.info). The average chemical composition (15 point analyses), \( \text{ScO}_{3.07} \text{V}_{0.86} \text{Fe}_{0.12} \text{Al}_{0.01} \text{K}_{0.01} \text{H}_{2} \text{O} \), was determined with a CAMECA SX50 electron microprobe (http://rruff.info). All crystals examined are severely twinned, with the twin axis along \( a \). Kolkbeckite crystals from another locality, viz., Christy Pit, Magnet Cove, Arkansas, USA (RRUFF deposition no. R061040), display the same feature.

Crystal data

\[
\text{ScPO}_4 \cdot 2\text{H}_2\text{O}
\]

\( M_r = 175.96 \)

Monoclinic, \( P_2_1/n \)

\( a = 5.4228 \) Å

\( b = 10.2027 \) Å

\( c = 8.9074 \) Å

\( \beta = 90.502^\circ \)

\( V = 493.08 \) Å\(^3\)

\( Z = 4 \)

Mo Ka radiation

\( \mu = 1.76 \text{ mm}^{-1} \)

\( T = 293 \) K

\( 0.07 \times 0.06 \times 0.06 \text{ mm} \)

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(SADABS, Sheldrick, 2005)

\( T_{\text{min}} = 0.887, T_{\text{max}} = 0.902 \)

Refinement

\[ R(F^2) = 0.052 \quad \text{H atoms treated by a mixture of independent and constrained refinement} \]

\( S = 1.11 \)

1885 reflections

\( \Delta \rho_{\text{max}} = 1.13 \text{ e Å}^{-3} \)

90 parameters

\( \Delta \rho_{\text{min}} = -1.21 \text{ e Å}^{-3} \)

Table 1

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O5–H1A</td>
<td>0.78 (6)</td>
<td>1.89 (6)</td>
<td>2.658 (5)</td>
<td>169 (10)</td>
</tr>
<tr>
<td>O5–H1B</td>
<td>0.78 (6)</td>
<td>1.95 (6)</td>
<td>2.704 (5)</td>
<td>165 (10)</td>
</tr>
<tr>
<td>O6–H2A</td>
<td>0.81 (5)</td>
<td>2.16 (5)</td>
<td>2.874 (5)</td>
<td>147 (9)</td>
</tr>
<tr>
<td>O6–H2B</td>
<td>0.80 (6)</td>
<td>2.27 (6)</td>
<td>3.029 (7)</td>
<td>168 (10)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \(-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2} \)

The twin refinement with the twin law \( (100, 0\overline{1}0, 0\overline{0}T) \) reduced the \( R_\text{I} \) factor from 0.105 to 0.052. The chemical analysis showed the presence of small amounts of \( \text{V}^{3+}, \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) in the sample, but the final refinement assumed a full occupancy of the octahedral site by \( \text{Sc}^{3+} \) only, as the overall effects of these trace amounts of elements on the final structure results are negligible. Four \( \text{H} \) atoms were located in the difference Fourier syntheses and their positions refined freely. The isotropic displacement parameters of the \( \text{H} \) atoms, however, were refined with the constraint that the \( U_{\text{iso}} \) values of atoms \( \text{H1A} \) and \( \text{H1B} \) were 1.2 times \( U_{\text{eq}} \) of their parent atom \( \text{O5} \), and those of atoms \( \text{H2A} \) and \( \text{H2B} \) were 1.2 times \( U_{\text{eq}} \) of their parent atom \( \text{O6} \). The highest residual peak in the difference Fourier map was located at \( (0.248, 0.662, 0.740) \), 1.28 Å from atom \( \text{O3} \), and the deepest hole at \( (0.100, 0.831, 0.252) \), 0.45 Å from \( \text{Sc1} \).

Data collection: \( \text{APEX2} \) (Bruker, 2003); cell refinement: \( \text{SAINT} \) (Bruker, 2005); data reduction: \( \text{SAINT} \); program(s) used to solve structure: \( \text{SHELXS97} \) (Sheldrick, 1997); program(s) used to refine structure: \( \text{SHELXL97} \) (Sheldrick, 1997); molecular graphics: \( \text{XtalDraw} \) (Dows & Hall-Wallace, 2003); software used to prepare material for publication: \( \text{SHELXL} \) (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA5100). Services for accessing these data are described at the back of the journal.

References


Sheldrick, G. M. (1997). \( \text{SHELXS97} \) and \( \text{SHELXL97} \). University of Göttingen, Germany.


