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Kolbeckite, $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$, isomorphous with metavariscite

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This study presents the first structural report of kolbeckite, with the ideal formula $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$ (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 $\text{ScO}_4(\text{H}_2\text{O})_2$ octahedra and *vice versa*, forming a three-dimensional network of polyhedra.

Comment

A number of phosphates and arsenates belong to the orthorhombic (*Pbca*) variscite and monoclinic ($P2_1/n$) metavariscite mineral groups with a general chemical formula $AXO_4 \cdot 2\text{H}_2\text{O}$, where $A = \text{Al}^{3+}$, Fe^{3+} , Sc^{3+} , In^{3+} or Ga^{3+} , and $X = \text{P}^{5+}$ 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: *Pbca* and $P2_1/n$ $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (Kniep & Mootz, 1973; Kniep *et al.*, 1977), *Pbca* and $P2_1/n$ $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (Moore, 1966; Song *et al.*, 2002; Taxer & Bartl, 2004), $P2_1/n$ $\text{In}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (Sugiyama *et al.*, 1999; Tang *et al.*, 2002), *Pbca* $\text{Al}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ (Harrison, 2000), $\text{Fe}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ (Hawthorne, 1976), $\text{In}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ (Tang *et al.*, 2002), and $\text{Ga}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (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 $\text{Sc}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ 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 (Schrauf, 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 $\text{ScO}_4(\text{H}_2\text{O})_2$ octahedra. Each PO_4 tetrahedron shares four vertices with four $\text{ScO}_4(\text{H}_2\text{O})_2$ octahedra and *vice versa*, forming a three-dimensional network of polyhedra (Fig. 1). The two H_2O molecules (O5 and O6) coordinated to Sc^{3+} are in *cis* positions, and the $\text{Sc}-\text{O}5$ and $\text{Sc}-\text{O}6$ distances are noticeably longer than the other four $\text{Sc}-\text{O}$ bond lengths. The average interatomic $\text{P}-\text{O}$ (1.527 Å) and $\text{Sc}-\text{O}$ (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 underbonded (4.926 valence units, v.u.), whereas Sc^{3+} is overbonded (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 $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (Kniep & Mootz, 1973), $\text{In}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (Sugiyama *et al.*, 1999) and $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (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 $\text{Sc}1-\text{O}5$ and $\text{Sc}1-\text{O}6$ bond distances of 2.116 (4) and 2.178 (4) Å, respectively, are significantly different, indicating distinct bonding environments for the two H_2O molecules. In fact, the hydrogen bonds involving atoms H1A and H1B are both shorter than those involving atoms H2A and H2B.

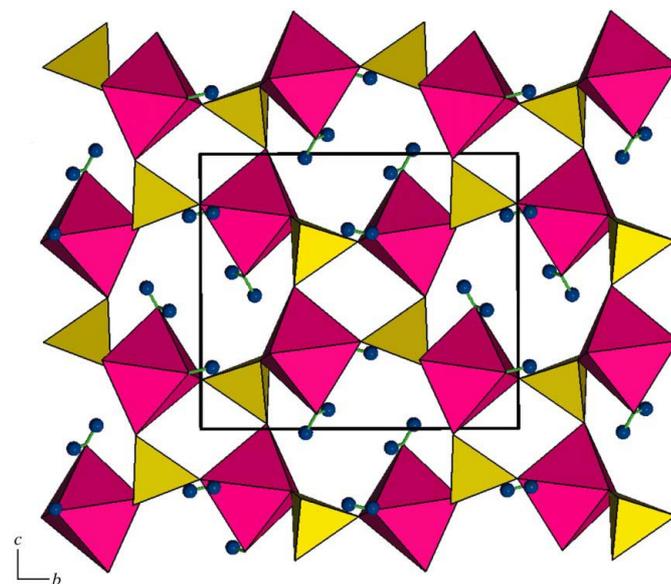


Figure 1

The crystal structure of kolbeckite, viewed along the *a* axis. The tetrahedra and octahedra represent the PO_4 and $\text{ScO}_4(\text{H}_2\text{O})_2$ groups, respectively. Small spheres indicate the H atoms.

Experimental

The kolbeckite 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), $(\text{Sc}_{0.94}\text{V}_{0.03}^{3+}\text{Fe}_{0.02}^{3+}\text{Al}_{0.01})_{\Sigma=1}\text{P}_{1.00}\text{O}_4 \cdot 2\text{H}_2\text{O}$, was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>). All crystals examined are severely twinned, with the twin axis along *a*. Kolbeckite crystals from another locality, viz. Christy Pit, Magnet Cove, Arkansas, USA (RRUFF deposition No. R061040), display the same feature.

Crystal data

ScPO ₄ ·2H ₂ O	<i>V</i> = 493.08 (7) Å ³
<i>M_r</i> = 175.96	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 5.4258 (4) Å	<i>μ</i> = 1.76 mm ⁻¹
<i>b</i> = 10.2027 (8) Å	<i>T</i> = 293 (2) K
<i>c</i> = 8.9074 (7) Å	0.07 × 0.06 × 0.06 mm
<i>β</i> = 90.502 (5)°	

Data collection

Bruker SMART CCD area-detector diffractometer	8954 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2005)	1858 independent reflections
<i>T_{min}</i> = 0.887, <i>T_{max}</i> = 0.902	1600 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.042

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.052	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.168	<i>Δρ_{max}</i> = 1.13 e Å ⁻³
<i>S</i> = 1.11	<i>Δρ_{min}</i> = -1.21 e Å ⁻³
1858 reflections	
90 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H1A···O1 ⁱ	0.78 (6)	1.89 (6)	2.658 (5)	169 (10)
O5—H1B···O4 ⁱⁱ	0.78 (6)	1.95 (6)	2.704 (4)	165 (10)
O6—H2A···O3 ⁱⁱⁱ	0.81 (5)	2.16 (6)	2.874 (5)	147 (9)
O6—H2B···O2	0.80 (6)	2.27 (6)	3.029 (7)	168 (10)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

The twin refinement with the twin law (100, 0 $\bar{1}$ 0, 00 $\bar{1}$) reduced the *R*₁ factor from 0.105 to 0.052. The chemical analysis showed the presence of small amounts of V³⁺, Fe³⁺ and Al³⁺ in the sample, but the final refinement assumed a full occupancy of the octahedral site by Sc³⁺ only, as the overall effects of these trace amounts of elements on the final structure results are negligible. Four H atoms were located in the difference Fourier syntheses and their positions

refined freely. The isotropic displacement parameters of the H atoms, however, were refined with the constraint that the *U*_{iso} values of atoms H1A and H1B were 1.2 times *U*_{eq} of their parent atom O5, and those of atoms H2A and H2B were 1.2 times *U*_{eq} of their parent atom O6. The highest residual peak in the difference Fourier map was located at (0.248, 0.662, 0.740), 1.28 Å from atom O3, and the deepest hole at (0.100, 0.831, 0.252), 0.45 Å from Sc1.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Xtal-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3100). Services for accessing these data are described at the back of the journal.

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