INTRODUCTION

The structures of brandholzite (Friedrich et al. 2000), Mg(H₂O)₆[Sn(OH)₆]₂, and bottinoite (Bonazzi and Mazzi 1996), Ni(H₂O)₆[Sn(OH)₆]₂, are isotypic and composed of isolated M²⁺(H₂O)₆ (M²⁺ = Mg, Ni) and Sn(OH)₆ octahedra, which are interconnected by hydrogen bonds. The octahedra are arranged in two types of layers which are stacked along the c axis. One layer consists of only Sn(OH)₆, octahedra, the other of Mg²⁺(H₂O)₆ and Sn(OH)₆, octahedra with an M²⁺/Sn-ratio of 2:1.

The crystal structure of synthetic Co(H₂O)₆[Sn(OH)₆]₂ was described as “pseudo-isotypic” (Friedrich et al. 2000) to the structures of natural and synthetic Mg(H₂O)₆[Sn(OH)₆]₂ and Ni(H₂O)₆[Sn(OH)₆]₂. Co(H₂O)₆[Sn(OH)₆]₂ showed a significant rotation around the threefold axis of two pairs of Sn(OH)₆ octahedra located at special positions at 1/3, 2/3, 1/3, z, with z = 0, 1/2. The rotations were attributed to different packing requirements due to the different sizes of the M²⁺(H₂O)₆ octahedra, which resulted in smaller unit-cell dimensions for Co(H₂O)₆[Sn(OH)₆]₂, in spite of the larger volume of the Co(H₂O)₆ octahedra compared to the Mg(H₂O)₆ octahedra.

DISCUSSION

A further analysis revealed that isotypism of the Co compound with brandholzite becomes evident by a shift of the origin of the previously described unit cell onto 2/3, 1/3, 0. The ten independent octahedra of the M²⁺(H₂O)₆[Sn(OH)₆]₂ structures are arranged in only four orientations (b, p, d, q) compared to the a axes (Bonazzi and Mazzi 1996). Calculating the octahedral rotational angles (according to Bonazzi and Mazzi 1996) for the Co compound, this gives orientations of b for the Sb₂ octahedron and the Sb₃ for the Sb⁴ octahedron in the layer z = 0, and d for Sb₅ and q for Sb₆ in z = 1/2, respectively. However, the Sb₂ octahedron should show p orientation, Sb₃ b, Sb₅ q, and Sb₆ d when compared to the structures of the Mg and Ni compounds. This discrepancy resulted in apparent rotation angles for these octahedra of about 29° (2x, in z = 0), and about 48° and 50° (in z = 1/2) in the Co compound relative to brandholzite (Friedrich et al. 2000). These angles correspond to the transformations of b in p and q in d, respectively, when

\[ x' = 2x - 1, 
\[ y' = 2y - 1, 
\[ z' = 2z - 1 \]

Note: Transformation of the coordinates by \( x' = 2x - 1, y' = 2y - 1, z' = 2z - 1 \) in order to transform the coordinates of Sb₂ (old) into Sb₁ (new) at (000).

* Transformed labeling for comparison with brandholzite and bottinoite after origin shift.
† Labeling used in Friedrich et al. (2000).

ADDITION

Isotypism of Co(H₂O)₆[Sn(OH)₆]₂ with brandholzite and bottinoite

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ABSTRACT

Isotypism of synthetic Co(H₂O)₆[Sn(OH)₆]₂ with brandholzite, Mg(H₂O)₆[Sn(OH)₆]₂, and bottinoite, Ni(H₂O)₆[Sn(OH)₆]₂, is obtained by an origin shift of the unit cell of Co(H₂O)₆[Sn(OH)₆]₂ (Friedrich et al. 2000) to 2/3, 1/3, 0.

INTRODUCTION

The structures of brandholzite (Friedrich et al. 2000), Mg(H₂O)₆[Sn(OH)₆]₂, and bottinoite (Bonazzi and Mazzi 1996), Ni(H₂O)₆[Sn(OH)₆]₂, are isotypic and composed of isolated M²⁺(H₂O)₆ (M²⁺ = Mg, Ni) and Sn(OH)₆ octahedra, which are interconnected by hydrogen bonds. The octahedra are arranged in two types of layers which are stacked along the c axis. One layer consists of only Sn(OH)₆, octahedra, the other of Mg²⁺(H₂O)₆ and Sn(OH)₆, octahedra with an M²⁺/Sn-ratio of 2:1.

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A further analysis revealed that isotypism of the Co compound with brandholzite becomes evident by a shift of the origin of the previously described unit cell onto 2/3, 1/3, 0. The ten independent octahedra of the M²⁺(H₂O)₆[Sn(OH)₆]₂ structures are arranged in only four orientations (b, p, d, q) compared to the a axes (Bonazzi and Mazzi 1996). Calculating the octahedral rotational angles (according to Bonazzi and Mazzi 1996) for the Co compound, this gives orientations of b for the Sb₂ octahedron and the Sb₃ for the Sb⁴ octahedron in the layer z = 0, and d for Sb₅ and q for Sb₆ in z = 1/2, respectively. However, the Sb₂ octahedron should show p orientation, Sb₃ b, Sb₅ q, and Sb₆ d when compared to the structures of the Mg and Ni compounds. This discrepancy resulted in apparent rotation angles for these octahedra of about 29° (2x, in z = 0), and about 48° and 50° (in z = 1/2) in the Co compound relative to brandholzite (Friedrich et al. 2000). These angles correspond to the transformations of b in p and q in d, respectively, when

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subtracting the $\phi$ angles observed in the Co compound (i.e., $73.6 - 45.6 = 28.0^\circ$, and $120 + 24.2 - 95.4 = 48.8^\circ$), and vice versa for the opposite rotations. Therefore, the above rotations of octahedra are equivalent to the interchange of $p$ with $b (z = 0)$ and $q$ with $d (z = 1/2)$ at $1/3, 2/3, z$ and $2/3, 1/3, z$, respectively. This result is obtained by shifting the origin of the unit cell to $2/3, 1/3, 0$ (Fig. 1).

Both the data collection and data reduction procedure were the same for Mg(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ and Co(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ (Friedrich et al. 2000). The starting parameters for the SHELXL-97 (Sheldrick 1997) structure refinement of the Co compound were obtained from the refined values for brandholzite. However, the resulting parameters differed in terms of a rotation of some octahedra as caused by a shift of the origin. The authors are not sure why the parameters shifted during the refinement, so that the setting changed, although the same starting parameters were used. $\{10\bar{1}0\}$ twinning and the strong pseudo-symmetry toward Laue class $3\bar{1}m$ (Bonazzi and Mazzi 1996), while the correct space group is $P3$, could be responsible for the different pathways followed by the SHELXL program in refining the synthetic Co compound.

**REFERENCES CITED**

