ADDENDUM

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

ALEXANDRA FRIEDRICH,[1] FIORENZO MAZZI,[2] MANFRED WILDNER,[1,*] AND EKKEHART TILLMANNS[1]

[1] Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria
[2] Dipartimento di Scienze della Terra, Università degli Studi di Pavia, Via Ferrata 1, I-27100 Pavia, Italy

ABSTRACT

Isotypism of synthetic Co(H₂O)₆[Sb(OH)₆]₂ with brandholzite, Mg(H₂O)₆[Sb(OH)₆]₂, and bottinoite, Ni(H₂O)₆[Sb(OH)₆]₂, is obtained by an origin shift of the unit cell of Co(H₂O)₆[Sb(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[Sb(OH)₆]₂, and bottinoite (Bonazzi and Mazzi 1996), Ni(H₂O)₆[Sb(OH)₆]₂ are isotypic and composed of isolated $M^{2+}(H_2O)_6$ (M^{2+} = Mg,Ni) and Sb(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 Sb(OH)₆ octahedra, the other of $M^{2+}(H_2O)_6$ and Sb(OH)₆ octahedra with an M^{2+}/Sb-ratio of 2:1.

The crystal structure of synthetic Co(H₂O)₆[Sb(OH)₆]₂ was described as "pseudo-isotypic" (Friedrich et al. 2000) to the structures of natural and synthetic Mg(H₂O)₆[Sb(OH)₆]₂ and Ni(H₂O)₆[Sb(OH)₆]₂. Co(H₂O)₆[Sb(OH)₆]₂ showed a significant rotation around the threefold axis of two pairs of Sb(OH)₆ octahedra located at special positions at 1/3, 2/3, z and 2/3, 1/3, z, with $z \approx 0$, 1/2. The rotations were attributed to different packing requirements due to the different sizes of the $M^{2+}(H_2O)_6$ octahedra, which resulted in smaller unit-cell dimensions for Co(H₂O)₆[Sb(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 $M^{2+}(H_2O)_6[Sb(OH)_6]_2$ 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 φ (according to Bonazzi and Mazzi 1996) for the Co compound, this gives orientations of **b** for the Sb2 octahedron and **p** for the Sb3 octahedron in the layer $z \approx 0$, and **d** for Sb5 and **q** for Sb6 in $z \approx 1/2$, 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° (2×, in $z \approx 0$), and about 48° and 50° (in $z \approx 1/2$) 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

TABLE 1. Revised atomic coordinates and isotropic displacement parameters for Co(H₂O)₆[Sb(OH)₆]₂

new*	old†	*x/a*	*y/b*	*z/c*	U_{eq}
			layer at z ≈ 0		
Sb1	Sb2	0	0	0.00000(7)	0.0116(1)
Sb2	Sb3	2/3	1/3	−0.08368(6)	0.0118(1)
Sb3	Sb1	1/3	2/3	0.00850(0)	0.0107(1)
Co1	Co1	0.33709(7)	0.00798(6)	−0.02739(13)	0.0165(2)
Co2	Co2	0.66237(7)	−0.00787(7)	−0.04322(11)	0.0146(2)
O1	O3	0.0334(3)	0.1138(3)	−0.1125(5)	0.0196(8)
O2	O4	0.1128(3)	0.0839(3)	0.1116(4)	0.0175(8)
O3	O6	0.5832(3)	0.2211(3)	−0.1977(5)	0.0205(9)
O4	O5	0.6958(3)	0.2494(3)	0.0281(4)	0.0189(8)
O5	O2	0.3035(3)	0.5522(3)	0.1212(4)	0.0183(8)
O6	O1	0.3628(2)	0.7803(3)	−0.1033(4)	0.0168(7)
O7	O9	0.3102(3)	0.0962(3)	−0.1573(5)	0.0254(10)
O8	O10	0.4274(3)	0.1173(3)	0.0960(5)	0.0280(10)
O9	O11	0.4550(3)	0.0350(3)	−0.1517(5)	0.0210(9)
O10	O12	0.3635(3)	−0.0851(3)	0.0897(5)	0.0206(9)
O11	O7	0.2520(3)	−0.1087(3)	−0.1564(5)	0.0222(9)
O12	O8	0.2193(3)	−0.0246(3)	0.0901(5)	0.0234(10)
O13	O17	0.5753(3)	0.0216(3)	0.0777(5)	0.0219(9)
O14	O18	0.6943(3)	0.1132(3)	−0.1603(5)	0.0180(8)
O15	O13	0.7804(3)	0.0789(3)	0.0733(5)	0.0195(8)
O16	O14	0.7536(3)	−0.0295(3)	−0.1743(5)	0.0195(9)
O17	O15	0.6322(3)	−0.1277(3)	0.0702(6)	0.0248(10)
O18	O16	0.5493(4)	−0.0966(4)	−0.1702(5)	0.0291(11)
			layer at z ≈ 1/2		
Sb4	Sb5	0	0	0.49683(7)	0.0119(1)
Sb5	Sb6	2/3	1/3	0.42075(8)	0.0106(1)
Sb6	Sb4	1/3	2/3	0.50470(8)	0.0104(1)
Sb7	Sb7	0.32782(3)	−0.00676(3)	0.47200(5)	0.0125(1)
Sb8	Sb8	0.66765(3)	0.00622(3)	0.45316(5)	0.0100(1)
O19	O22	0.0652(3)	0.1141(3)	0.3752(4)	0.0160(7)
O20	O21	0.1143(3)	0.0415(3)	0.6112(4)	0.0175(8)
O21	O23	0.5517(3)	0.2670(3)	0.5407(5)	0.0163(8)
O22	O24	0.6211(3)	0.2188(3)	0.3058(4)	0.0175(8)
O23	O20	0.2644(3)	0.5521(3)	0.6184(4)	0.0172(8)
O24	O19	0.3950(2)	0.7812(2)	0.3836(4)	0.0147(7)
O25	O27	0.2615(3)	0.0418(3)	0.3510(5)	0.0176(8)
O26	O28	0.3742(3)	0.1114(3)	0.5790(4)	0.0171(8)
O27	O29	0.4433(3)	0.0572(3)	0.3536(5)	0.0162(8)
O28	O30	0.3973(3)	−0.0504(3)	0.5889(5)	0.0174(8)
O29	O25	0.2801(3)	−0.1234(3)	0.3559(5)	0.0165(8)
O30	O26	0.2123(3)	−0.0727(3)	0.5852(5)	0.0166(8)
O31	O35	0.6204(3)	0.0738(3)	0.5708(5)	0.0180(8)
O32	O36	0.7339(3)	0.1189(3)	0.3301(5)	0.0168(8)
O33	O31	0.7833(3)	0.0590(3)	0.5660(5)	0.0170(8)
O34	O32	0.7091(3)	−0.0653(3)	0.3355(5)	0.0161(8)
O35	O33	0.6075(3)	−0.1079(3)	0.5724(4)	0.0181(8)
O36	O34	0.5497(3)	−0.0425(3)	0.3421(4)	0.0162(8)

Note: Transformation of the coordinates by $x − 2/3$, $y − 1/3$, $z + 0.0085$ 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).

---

* E-mail: manfred.wildner@univie.ac.at
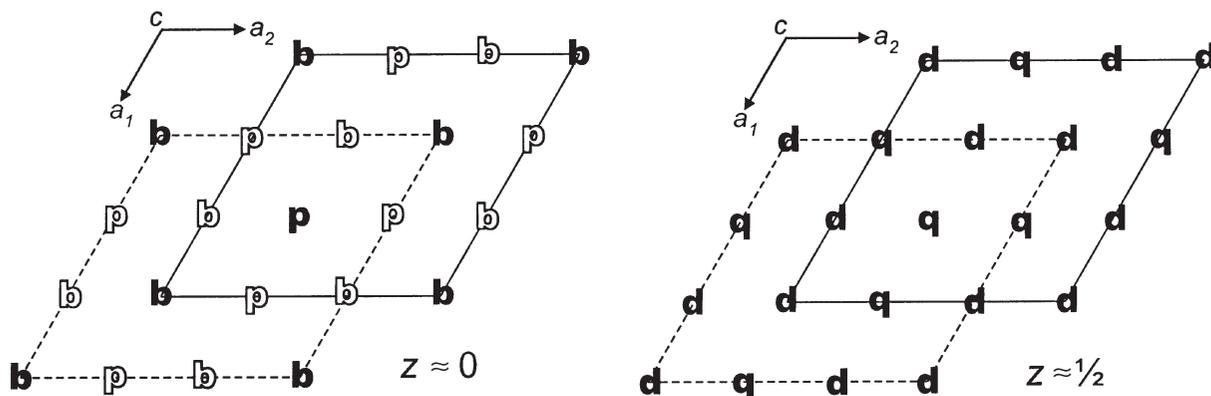
FIGURE 1. Mutual orientation of octahedra schematically indexed (see text). Projection of the mixed $\{[Sb(OH)_6]_3[M^{2+}(H_2O)_6]_6\}^{9+}$ layer (at z $\approx$ 0) and the $\{[Sb(OH)_6]_9\}^{9-}$ layer (at z $\approx$ 1/2) on (0001). The unit cell with the dashed line refers to the setting of $Co(H_2O)_6[Sb(OH)_6]_2$ used by Friedrich et al. (2000), that with the solid line to the new one, corresponding to the Mg and Ni compound. Solid letters refer to Sb octahedra, open letters to M^{2+} octahedra.

subtracting the ϕ angles observed in the Co compound (i.e., 73.6 – 45.6 = 28.0°, and 120 + 24.2 – 95.4 = 48.8°), and vice versa for the opposite rotations. Therefore, the above rotations of octahedra are equivalent to the interchange of **b** with **p** (z $\approx$ 0) and **q** with **d** (z $\approx$ 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 $Mg(H_2O)_6[Sb(OH)_6]_2$ and $Co(H_2O)_6[Sb(OH)_6]_2$ (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 $\bar{3}1m$ (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

Bonazzi, P. and Mazzi, F. (1996) Bottinoite, $Ni(H_2O)_6[Sb(OH)_6]_2$: Crystal structure, twinning, and hydrogen bond model. American Mineralogist, 81, 1494–1500.
Friedrich, A., Wildner, M., Tillmanns, E., and Merz, P.L. (2000) Crystal chemistry of the new mineral brandholzite, $Mg(H_2O)_6[Sb(OH)_6]_2$, and of the synthetic analogues $M^{2+}(H_2O)_6[Sb(OH)_6]_2$ (M^{2+} = Mg, Co). American Mineralogist, 85, 593–599.
Sheldrick, G.M. (1997) SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany.