

**CRYSTAL STRUCTURES OF ACENTRIC AND CENTROSYMMETRIC
MEMBERS OF THE $A^2Me^{2+}_3(OH)_2(SO_4)_3 \cdot 2H_2O$ -GROUP**

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The crystal structures of synthetic compounds with the general formula $A^2Me^{2+}_3(OH)_2(SO_4)_3 \cdot 2H_2O$ were at first described by LOUER & LOUER (1982) (A-Me = K-Cd, Cs-Cd) and EFFENBERGER & LANGHOF (1984) (K-Co) in the acentric ortho-rhombic space group $Cmc2_1$. In the course of syntheses experiments in the system (Na, K, Rb, Cs, NH₄, Ag)-(Co, Ni)-(S, Se) aiming at the preparation of natrochalcite-type compounds, several representatives belonging to the above mentioned group were obtained. Syntheses runs were performed under low-hydrothermal conditions in Teflon-lined steel vessels at a temperature of 220°C and a runtime of a week, starting with the respective metal powders covered with A₂SO₄, H₂SO₄ and H₂O. The structures were determined (or refined in the case of K-Co) from single crystal X-ray CCD data. The following Table lists relevant crystal data:

A-Me-X	SG	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<A ^{[x].O} > (Å)	Me(1) ^{[6].O} (Å)	Me(2) ^{[6].O} (Å)
K-Ni	<i>Cmc2</i> ₁	17.899	7.462	9.699	2.994, x = [9+1]	2.054-2.144	2.041-2.093
Rb-Ni	<i>Cmc2</i> ₁	18.229	7.536	9.761	3.065, x = [9+1]	2.059-2.137	2.055-2.096
K-Co	<i>Cmc2</i> ₁	17.960	7.565	9.768	2.977, x = [9]	2.092-2.189	2.058-2.143
NH ₄ -Co	<i>Cmc2</i> ₁	18.267	7.595	9.814	3.069, x = [10]	2.087-2.172	2.077-2.154
Rb-Co	<i>Cmc2</i> ₁	18.274	7.639	9.832	3.081, x = [9+1]	2.089-2.178	2.074-2.150
Cs-Co	<i>Pm</i> <i>cn</i>	18.826	7.837	9.869	3.263, x = [9+2]	2.070-2.167	2.103-2.213

The crystal structures are composed of two crystallographically different types of moderately distorted MeO₆ octahedra, two types of SO₄ tetrahedra, and one distinct A position. The Me(1)O₆ groups share edges forming octahedral dimers, which are linked via common corners with the Me(2)O₆ groups to infinite polar zig-zag chains parallel to the (polar) *c*-axis. These chains are linked by SO₄ tetrahedra and hydrogen bonds to form [Me₃(OH)₂(SO₄)₃(H₂O)₂]²⁻ sheets parallel to (100). The A cations as well as a further hydrogen bond connect adjacent sheets along the *a*-axis. In the acentric representatives, all octahedral chains are oriented with parallel polarity. Contrary, as a special feature of the cesian-cobalt compound, adjacent sheets are rotated by 180°, thus leading to an anti-parallel arrangement of the polar chains in neighbouring sheets. The resulting symmetry is centrosymmetric and loses the former C-centering, resulting in space group *Pm**cn* (conventional setting: *Pnma*). The investigation of further representatives as well as of an obviously related Ag-Co compound (orthorhombic *P* with *a*' = 2/3*a*, *b*' = *b*, *c*' = *c*) is in progress.

References

- EFFENBERGER, H. & LANGHOF, H. (1984): *Monatsh. Chem.*, 115, 165-177.
LOUER, M. & LOUER, D. (1982): *Rev. Chim. Mineral.*, 19, 162-171.