

**A COMPARATIVE STUDY OF X-RAY DIFFRACTION RESULTS OBTAINED
25 YEARS APART: THE CRYSTAL STRUCTURE OF $\text{Co}_2(\text{OH})_2(\text{SeO}_3)$ FEATURING
 $\text{O}-\text{H}\cdots E[\text{Se}^{4+}]$ HYDROGEN BONDS ($E = \text{LONE ELECTRON PAIR}$)**

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Only about a century ago, in 1912, Max von Laue and co-workers established the basis for the structure investigation of crystalline materials by demonstrating the diffraction of X-rays at the ordered atomic arrangement in crystals. Naturally, experimental and, later, computational methods have evolved dramatically since then, and, with the wide availability of automatic four-circle diffractometers since the 1980ies, the number of published crystal structures increases exponentially. But also within this later period, experimental methods and refinement strategies were – and constantly are, of course – further developed and improved. Within the framework of a Bachelor thesis (KREMLICKA, 2017), we reinvestigated the unpublished crystal structure of $\text{Co}_2(\text{OH})_2(\text{SeO}_3)$, a simple but crystal chemically very interesting compound, using the very same single crystal synthesized and investigated already in 1991 (WILDNER, 1995). Both data sets were obtained on four-circle diffractometers, the earlier using a point detector (3795 reflections measured) with refinement on 1508 unique $F_o > 3\sigma(F_o)$, the new one using a CCD area detector (7156 reflections measured) with refinement on all 1889 unique F_o^2 .

$\text{Co}_2(\text{OH})_2(\text{SeO}_3)$ crystallizes monoclinic ($P2_1/n$, $a = 7.724(1)$, $b = 5.829(1)$, $c = 9.568(2)$ Å, $\beta = 97.37(1)^\circ$, $V = 427.2(1)$ Å³, $Z = 4$) and is built from complex sheets of two types of strongly distorted face-, edge- and corner-sharing CoO_6 octahedra, which are interlinked via SeO_3 groups and ‘standard’ $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (2.730 Å). A second type of H atom forms no obvious hydrogen bond, but is pointing towards the Se-apex of the pyramidal selenite group, with $\text{O}\cdots\text{Se} = 4.104$ Å; however, calculating the position of the Se^{4+} apical lone electron pair E (KOSKENLINNA, 1996) yields $\text{Se}-E = 1.38$ Å, resulting in a possible, nearly linear, $\text{O}-\text{H}\cdots E$ hydrogen bond with $\text{O}\cdots E = 2.91$ Å. Concerning this unusual finding, a literature search is in progress, but so far no comparable cases were found.

The comparison of the two structure analyses from 1991 and 2017 reveals a generally good agreement of the positional atomic parameters for oxygen and heavier atoms; i.e. $\text{Se}-\text{O}$ and $\text{Co}-\text{O}$ distances and angles usually match within $1-2\sigma$, whereas, e.g., displacement parameters differ quite dramatically (with much higher values for the data from 1991), albeit showing similar tendencies concerning anisotropy. These findings might indicate that also other non-positional refinement parameters, e.g. atomic site occupancies essential in structure refinements of minerals (and solid solutions in general), could differ significantly for the very same sample throughout ‘modern’ structure analyses (i.e. based on four-circle diffractometer data) which have been performed around a quarter-century apart.

KOSKENLINNA, M. (1996): Ann. Acad. Sci. Fenn. Chem., 262, 1-52.

KREMLICKA, T. (2017): Bacc. Thesis Univ. Wien, in preparation.

WILDNER, M. (1995): Z. Kristallogr. Suppl. Issue, 9, 248.