

Structure building properties of lone electron pairs

Structural/stereochemical lone pair requirements/activities can lead to different polymorphs as e.g. for $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$

New polymorphic and pseudosymmetrical cobalt selenite monohydrates, $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ II and $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ III

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Dedicated to Professor W. H. E. Schwarz on the occasion of his 60th birthday

Abstract. The crystal structures of two polymorphic, hydrothermally synthesized cobalt selenite monohydrates, $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ II ($a = 568.1(1)$ pm, $b = 476.7(1)$ pm, $c = 1348.0(2)$ pm, $\beta = 101.37(1)^\circ$) and $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ III ($a = 477.2(1)$ pm, $b = 1320.9(3)$ pm, $c = 568.6(1)$ pm, $\beta = 90.54(1)^\circ$), both $mP32$, $P2_1/n$, $Z = 4$, have been determined by single crystal X-ray diffraction. Both structures are built up from buckled *trans* layers $\infty^2[\text{CoSeO}_3 \cdot \text{H}_2\text{O}]$ consisting of strongly distorted $\text{CoO}_5(\text{H}_2\text{O})$ octahedra and trigonal pyramidal SeO_3^{2-} ions. The structures differ with respect to the stacking of the layers, which originates in their pseudosymmetry and in the stereochemical requirements of the selenite lone electron pair. Only intra-layer H bond schemes are built, i.e., the layers are held together by van der Waals interactions.

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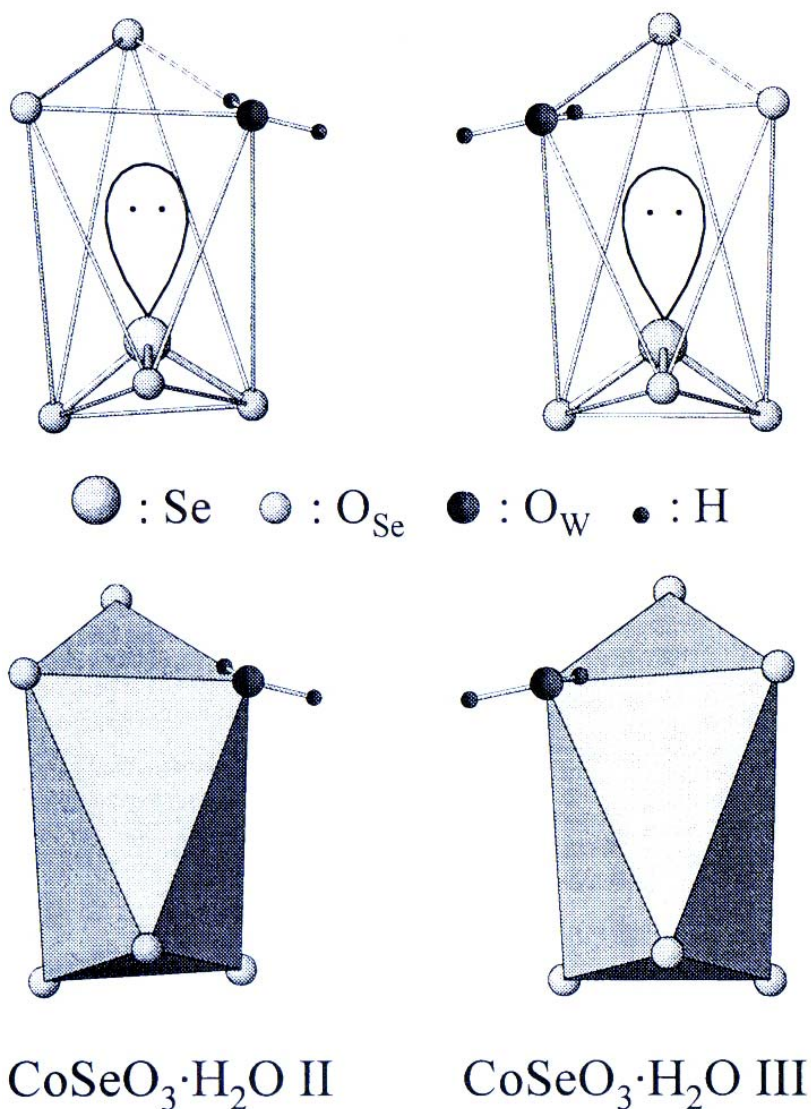


Fig. 5. Environments of the Se atoms between the $\frac{2}{\infty}[\text{CoSeO}_3 \cdot \text{H}_2\text{O}]$ layers of $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ II (viewed along $[010]$) and $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ III (viewed along $[100]$).

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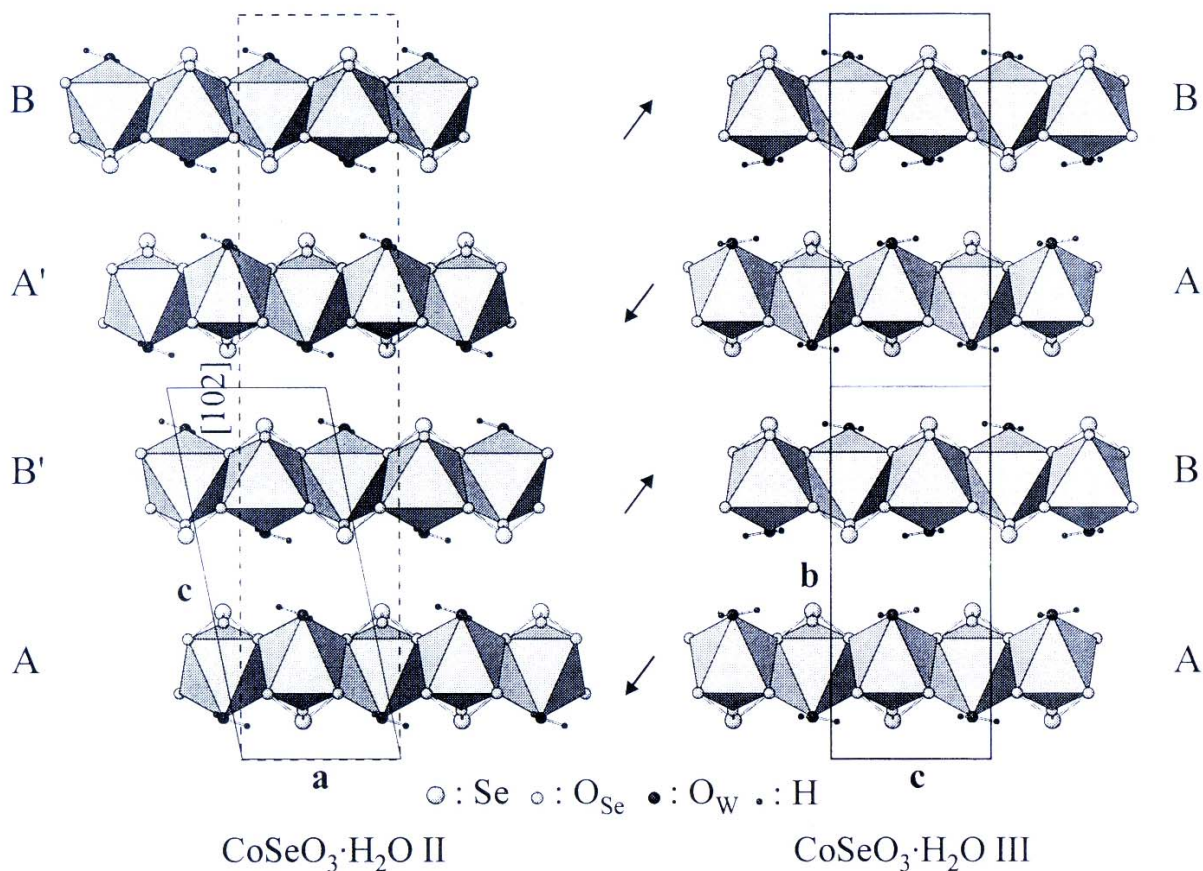


Fig. 4. Projections of the crystal structures of $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ II (along $[010]$) and $\text{CoSeO}_3 \cdot \text{H}_2\text{O}$ III (along $[100]$), showing the stacking of the layers $\frac{2}{\infty}[\text{CoSeO}_3 \cdot \text{H}_2\text{O}]$. Dashed lines belong to the pseudo-B centered cell of CoII. The arrows indicate the directions of the apical Se—O bonds in the respective layers.