

Crystal Structure and Thermal Properties of Cobalt Hydrogenselenite Dihydrate, $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$

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$\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ crystallizes in a monoclinic space group $P2_1/n$ with cell dimensions $a = 7.117(1)$, $b = 6.872(1)$ and $c = 8.018(2)$ Å, and $\beta = 113.17(2)^\circ$, $Z = 2$. R - and wR -values are 6.50 and 8.95, respectively, for 790 observed reflections. The cobalt ion coordination is slightly distorted octahedral with water molecules at the apexes at a distance of 2.110(4) Å. The basal plane is formed by four hydrogenselenite oxygen atoms with the distances of 2.061(4) and 2.130(5) Å. Each oxygen belongs to a different hydrogenselenite ion which bridges two cobalt ions, forming a two-dimensional layer-like structure. The Se–O distances within the hydrogenselenite ion are 1.660(5) and 1.662(4) Å, and 1.759(5) Å for the Se–OH distance. The protonated oxygen atom participates in hydrogen bonding, joining the adjacent layers with an O–O distance of 2.707(6) Å. Thermal decomposition proceeds via three intermediate phases to CoO, which is the end product. The IR spectrum was also recorded and interpreted.

Boutzoureano¹ described, in his thorough early study of metal selenites, the preparation of three different cobalt selenite compounds, for which he reported the formulae $3(\text{CoSeO}_3) \cdot \text{H}_2\text{O}$ and CoSe_2O_5 , but then gave for the third one two alternatives, $\text{CoSe}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ or $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$. The crystal structures of two of the above compounds have so far been reported, namely $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}^2$ and CoSe_2O_5 .^{3,4} In addition, several other structures of divalent cobalt selenites are known, viz. the structures of CoSeO_3 ,⁵ $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$,⁶ $\text{K}_2\text{Co}(\text{SeO}_3)_2$,⁷ $\text{K}_2(\text{Co}_2(\text{SeO}_3)_3) \cdot 2\text{H}_2\text{O}^8$ and $\text{NaCo}_2(\text{SeO}_3)_2(\text{OH})$.⁹

Gattow¹⁰ found that an isomorphous series of diselenite compounds exists with the formula $\text{MeSe}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, where Me is Co, Ni or Zn. Unit-cell dimensions of the series were given, but the reasons for the choice of formula were not discussed. On the other hand, Kondrashev *et al.*¹¹ described the crystal structure of $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$, based on neutron diffraction analysis. The volume of the unit cell used was approximately half that reported by Gattow for the Zn compound.¹⁰

We have now prepared and studied the structural properties of the cobalt compound which belongs to a group of metal selenites containing bridging bidentate selenite ligands.

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Experimental

Preparation of the compound. The dark violet compound $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ can be crystallized from a solution of H_2SeO_3 (> 1.0 M) into which CoCO_3 has been dissolved with molar ratios of Co to Se from 1:2 to 1:4. Crystallization takes place best by allowing the excess water to evaporate within 2–3 days at temperatures between 30 and 60°C. Very large crystals can thus be obtained. From more dilute solutions a dark red selenite dihydrate compound $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ can also be crystallized by allowing the solution to stand for a few days. Therefore care must be taken in order to distinguish the two phases, which under microscopic scrutiny resemble each other. The chemical properties of the compounds are different in that $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ readily dissolves in water and is degraded by ethanol. $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ is much less soluble and does not dissolve in water or ethanol during preparation.

Structure determination. A violet crystal of the title compound was mounted on a Nicolet P3 four-circle diffractometer controlled by Nova 3 computer. Unit-cell parameters were obtained by carefully centering 25 reflections with $20 > 2\theta > 25^\circ$ using $\text{MoK}\alpha$ ($\lambda = 0.71069$ Å) radiation. The data were corrected for Lorentz and polarization effects and empirically for absorption using a

psi-rotation method. Isotropic extinction correction was also applied. All calculations were done using a SHELXTL PLUS (PC version) software package.¹² Atomic scattering factors were those included in the program system used. Experimental details of data collection, structure determination and structure refinement are listed in Table 1.

IR and thermal measurements. The IR spectrum in the region 4000–300 cm⁻¹ was recorded with a Nicolet Magna-IR spectrometer 750 using the KBr and polyethylene pellet techniques.

Thermoanalytical measurements were carried out in a Seiko Instruments TG/DTA 320 analyzer, equipped with SSC5200 disk station in dynamic air and nitrogen

Table 1. Structure determination summary for Co(HSeO₃)₂·2H₂O.

Crystal data	
Empirical formula	H ₆ CoO ₈ Se ₂
Color	Violet
Crystal size mm	0.14 × 0.18 × 0.21
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit-cell dimensions	<i>a</i> = 7.117(1) Å <i>b</i> = 6.872(1) Å <i>c</i> = 8.018(2) Å <i>β</i> = 113.17(3) Å
Volume	360.5(2) Å ³
<i>Z</i>	2
Formula weight	350.9
Density (calc.)	3.232 Mg m ⁻³
Absorption coefficient	12.479 mm ⁻¹
<i>F</i> (000)	330
Data collection	
Diffractionmeter used	Nicolet P3
Radiation	MoK α (λ = 0.710 69 Å)
Temperature/K	298
Monochromator	Highly oriented graphite crystal
2 θ Range/°	3.0–53.0
Scan type	ω
Scan speed	Variable; 2.00 to 29.30° min ⁻¹ in ω
Scan range (ω)	1.0°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time
Standard reflections	3 measured every 100 reflections
Index ranges	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 8, -10 ≤ <i>l</i> ≤ 9
Reflections collected	888
Independent reflections	826 (<i>R</i> _{int} = 9.17%)
Observed reflections	790 [<i>I</i> ≥ 2.0 σ (<i>I</i>)]
Absorption correction	Empirical, Psi-rotation
Solution and refinement	
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Patterson method
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma(F_o - F_c)^2$
Extinction correction	$\chi = 0.037(3)$, where $F^* = [1 + 0.002\chi F^2 / \sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic <i>U</i>
Weighting scheme	$w^{-1} = \sigma^2(f) + 0.0075F^2$
Parameters refined	53
Formula <i>R</i>	$R = [\Sigma(F_o - F_c) / \Sigma F_o]$
Formula of weighted <i>R</i>	$wR = [\Sigma w^2(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$
<i>R</i> -Values (obs. data)	<i>R</i> = 6.50%, <i>wR</i> = 8.95%
<i>R</i> -Values (all data)	<i>R</i> = 6.60%, <i>wR</i> = 9.23%
Goodness-of-fit	1.02
Largest and mean Δ/σ	0.824, 0.132
Data-to-parameter ratio	14.9:1
Largest difference peak	2.52 e Å ⁻³
Largest difference hole	-1.99 e Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for nonhydrogen atoms of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Atom	x/a	y/b	z/c	U_{eq}^a
Co	5000	5000	5000	16(1)
Se	531(1)	2691(1)	3763(1)	18(1)
O(1)	-1088(7)	4526(8)	2425(7)	32(2)
O(2)	2569(6)	3325(6)	3368(5)	25(1)
O(3)	-374(6)	773(6)	2424(6)	22(1)
O(4)	6898(6)	2649(5)	4978(5)	24(1)

^aEquivalent isotropic U is of the form $U_{\text{eq}} = 1/3 (\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j)$.

atmospheres. Sample mass was 20 mg and the heating rate was $10^\circ \text{ min}^{-1}$. Standard platinum crucibles were employed, and aluminium oxide was used as a reference material.

Results and discussion

Crystal structure. The final atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms are listed in Table 2. Bond lengths and angles for nonhydrogen atoms are given in Table 3.[†] The structure with the atom labelling is shown in Fig. 1. Unit-cell packing in the b -axis direction is shown in Fig. 2. The structure is isostructural with $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ studied by neutron diffraction, in which hydrogen atom positions were refined as well.¹¹ The unit-cell data of the Zn compound are as follows: space group $P2_1/b$; $a = 7.155$, $b = 8.434$, $c = 6.888 \text{ \AA}$, $\gamma = 61.58^\circ$. In the present structure hydrogen atom positions of the water molecule could not be located clearly, so they were positioned as a riding model in the directions obtained from the neutron diffraction study of the isostructural Zn compound.

The coordination sphere around the cobalt ion is a slightly distorted octahedron with Co–O distances ranging from 2.061(4) to 2.130(5) \AA , slightly shorter than the Co–O distances in $\text{K}_2\text{Co}(\text{SeO}_3)_2$ [2.142(1) \AA]⁷ or in CoSeO_3 (2.076–2.214 \AA),⁵ but within the same range as in CoSe_2O_5 .⁴ The structure consists of two-dimensional layers perpendicular to the ac -plane. Each bridging hydrogen-selenite ion is coordinated to two different cobalt ions. These chains run along the diagonals of the unit cell $\text{Co}(0, 0, 0)$ –O2–Se–O3–Co($1/2, 1/2, 1/2$)–O3–Se–O2–Co(1, 1, 1) and $\text{Co}(0, 1, 0)$ –O3–Se–O2–Co($1/2, 1/2, 1/2$)–O2–Se–O3–Co(1, 0, 1).

The interatomic Se–O bond distances of 1.660(5) and 1.662(4) \AA and angles in the flattened pyramidal hydrogen-selenite ion agree well with those of the isostructural $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$; however, the Se–OH distance is 1.759(5) \AA in $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ and 1.786 \AA in

Table 3. Bond lengths (in \AA) and angles (in $^\circ$) for nonhydrogen atoms of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Co–O(2)	2.061(4)	O(2)–Co–O(4)	87.0(2)
Co–O(4)	2.110(4)	O(4)–Co–O(2)(i)	93.0(2)
Co–O(2)(i)	2.061(4)	O(2)–Co–O(3)(iii)	86.3(2)
Co–O(3)(ii)	2.130(5)	O(4)–Co–O(3)(ii)	82.7(2)
Co–O(3)(iii)	2.130(5)	O(2)–Co–O(3)(iii)	93.7(2)
Co–O(4)(i)	2.110(4)	O(4)–Co–O(3)(iii)	97.3(2)
Se–O(1)	1.759(5)	O(2)–Co–O(4)(i)	93.0(2)
Se–O(2)	1.660(5)	O(1)–Se–O(2)	96.2(2)
Se–O(3)	1.662(4)	O(1)–Se–O(3)	100.4(2)
		O(2)–Se–O(3)	103.3(2)
		Co–O(2)–Se	127.1(3)
		Co–O(3)(ii)–Se(iii)	129.1(3)

Symmetry codes refer to following equivalent positions: (i) $1-x, 1-y, 1-z$, (ii) $x-1/2, 1/2-y, z-1/2$ and (iii) $1/2-x, y-1/2, 1/2-z$.

$\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$.¹¹ The interatomic Se–O distances in selenite ions can vary from three practically equal distances of 1.719 and $(2 \times) 1.716 \text{ \AA}$, as found in CoSeO_3 to 1.751 and $(2 \times) 1.695 \text{ \AA}$ in CuSeO_3 .⁵ Based on a survey of selenite structure, the mean values for interatomic distances and angles for HSeO_3 have been found to be 1.706 \AA for Se–O and 1.762 \AA for Se–OH distances and 99.6° for O–Se–O angle.¹³

A three-dimensional network is formed by hydrogen bonds. The oxygen atom O4 of the water molecule is hydrogen-bonded to two oxygen atoms, the protonated selenite oxygen atom O(1) ($1/2-x, y-1/2, 1/2-z$) and the coordinated oxygen atom O(2) ($1/2+x, 1/2-y, 1/2+z$) with the distances 2.789(6) and 2.654(6) \AA , respectively. These hydrogen bonds are within the layers. The proton-

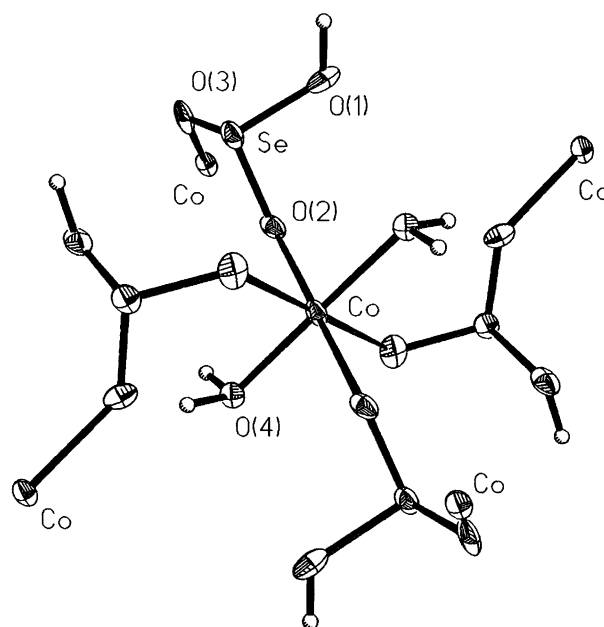


Fig. 1. The structure of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ showing coordination spheres of cobalt ions and the bridging hydrogen-selenite ion with atomic labelling. Thermal ellipsoids are drawn on 50% probability level.

[†] Lists of structure factors, anisotropic displacement parameters and H-atom positions are available from one of the authors (J. K.).

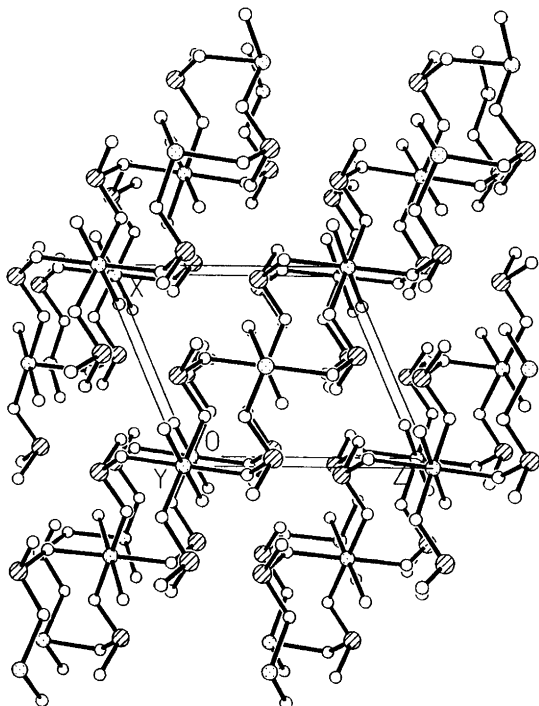


Fig. 2. Unit-cell packing of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ in the b -axis direction showing the layered structure. Hydrogen atoms are omitted for clarity.

ated oxygen atom O(1) is additionally hydrogen-bonded to the coordinated oxygen atom O(3) ($-x - 1/2, 1/2 + y, 1/2 - z$) of the adjacent layer with the distance 2.707(6) Å, thus joining the layers together. The O4–O2 and O4–O1 distances of the water oxygen atom to the hydrogen-selenite oxygen atoms are equal within 1σ compared to those in the isostructural $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$, but the O1–O3 distance is 0.050 Å longer in the Co compound.

Thermal analysis. Thermal decomposition proceeds in a remarkably similar fashion both in air and in nitrogen. There are three major plateaus in both cases, namely at 400°C, at around 480–530°C and 600–630°C onwards, with a fourth minor nick at 830–930°C. Figure 3 shows the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ in air. Decomposition starts by loss of water and some SeO_2 in three distinctive endothermic steps before the first plateau. The first step at 130°C corresponds most likely to a loss of water of crystallization (obs. 10%, calc. 10.3%). This is followed by an additional loss of water originating from the hydrogen-selenite hydroxyl groups and also some SeO_2 in two steps before the first plateau is reached at 400°C. Weight loss to the first plateau is 20.3 and 20.8% in air and nitrogen, respectively. If it is presumed that all water is lost by then, it can be calculated that approximately 0.15 mol of SeO_2 is expelled per mole of the starting compound. This decomposition mechanism would imply the presence of both diselenite and selenite in the solid resi-

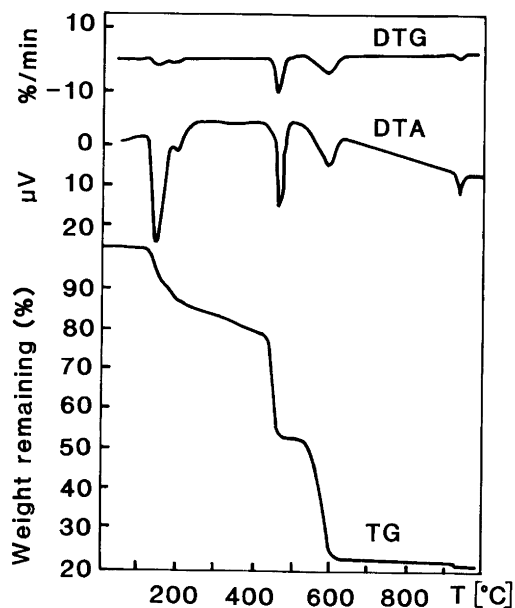


Fig. 3. TG, DTG and DTA curves of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ in air.

due at this stage. A very similar scheme was observed for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, which was observed to lose 0.07 mol of SeO_2 per mole of starting compound by 360°C.¹⁴

The weight loss to the second plateau corresponds well to formation of CoSeO_3 , with observed weight losses of 47.0 and 47.7% in air and nitrogen, respectively, and a calculated value of 47.0%. CoSeO_3 was also found to form in the decomposition of CoSe_2O_5 at 500°C.⁴ The material of the second plateau is somewhat less stable in air than in nitrogen, with a further degradation of the material starting some 30°C earlier (at 500°C). A phase containing mostly CoO but also a minor amount of selenite is formed. Finally, CoO is formed with a loss of 1.8 and 1.7% in air and nitrogen, respectively. This weight change indicates that a phase containing 6–7% of SeO_2 per mole of Co is stable between ca. 630 and 830–930°C. Total weight loss was observed to be 78.6 and 78.9% in air and nitrogen, respectively, while the calculated value corresponding to the change from $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ to CoO is 78.6%.

Table 4. Infrared absorption frequencies in the region 4000–300 cm^{-1} .

Observed frequency	Assignment
3419 (vs, sh)	$\nu(\text{OH})$
3072 (s, br)	$\nu(\text{OH})$
1648 (m)	$\delta(\text{H}_2\text{O})$
1124 (m)	$\delta(\text{OH}, \text{Se-OH})$
846 (s) }	$\nu_1(\text{Se-O})$
806 (vs) }	
699 (s)	$\nu_3(\text{Se-O})$
617 (s)	$\nu(\text{Se-OH})$
495 (s)	$\nu_2(\text{O-Se-O})$
367 (m, sh) }	$\nu_4(\text{O-Se-O})$
357 (m) }	

IR spectrum. The IR spectrum of $\text{Co}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ displays vibrations due to the stretching and bending modes of H_2O and HSeO_3 . Table 4 presents the observed frequencies as well as an assignment of the vibrations. The present data complement the IR studies of cobalt selenites by Melnikova *et al.*,¹⁵ who investigated the $\text{CoSeO}_3 \cdot n\text{H}_2\text{O}$ ($n = 1, 2, 1/3$) compounds.

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